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Olefins isomerization by hydride-complexes of ruthenium

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Abstract

Several complexes containing the Ru–H bond were synthesized according to previous reports: $RuH(NO)(PPh_3)_3(I)$ (**1**), $RuHCl(PPh_3)_3(s)(II)$ (**2**), $RuHCl(CO)(PPh_3)_3(II)$ (**3**), $RuH(CH_3COO)(PPh_3)_3(II)$ (**4**) and $RuH_2(CO)(PPh_3)_3(II)$ (**5**), and characterized by ^1H NMR and IR spectra; the complex of $RuHCl(PPh_3)_3(s)$ was screened for further investigation on the basis of activity and life-operating on isomerization of 1-hexene and 1-octadecene in temperature; the influence of temperature, reaction time and catalyst concentration on 1-hexene isomerization by $RuHCl(PPh_3)_3(s)$ was carefully studied: 1-hexene was converted into other two isomers of 19.39% 2-hexene and 78.16% 3-hexene on the condition of catalyst 2×10^{-5} mol (in 1 ml toluene), temperature 120 °C, time 30 min, 1-hexene 4 ml; while the performance on 1-octadecene isomerization by $RuHCl(PPh_3)_3(s)$ presented high activity, thermal stability and the solvent-free system: at 180 °C the equilibrium conversion of 1-octadecene reached above 94.6% with the condition of the 1:200 (mol) ratio of catalyst to substrate; and the distinct differences were presented on the isomerization by $RuHCl(PPh_3)_3(s)$ for 1-hexene and 1-octadecene in reaction temperature, solvent, intermediate. The evidence on isomerization of 1-hexene and 1-octadcene by $RuHCl(PPh_3)_3(s)$ was provided to recognize the specifically isomerization process: the catalytic property was closely relation with coordination circumference of the centre metal, ligand property and substrate structure, and the mechanism was carefully studied on **2** as well.
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1. Introduction

Transition metal hydrides are important not only in organometallic chemistry but also in organic synthesis [1], recently the area has being attracted and rapidly developed on catalytic reactions with the feature of high activity and selectivity, mild reaction condition and substrate generality as well as the reaction process studied easily (homogeneous), some types of reaction is enumerated in this respect: the activating reaction of C–H bond and C–C bond, hydroformylation of olefin, hydrogenation of double bond, telomerisation of olefins and dienes, hydrosilication reaction, hydrogen transfer (TH) and isomerization reaction, etc., and being active species was always detected or proposed in the catalytic process of non-transition-metal-hydride as precursor, such as complexes of Co, Ni, Pd, Rh, Fe, Ru [2] among those, the hydride-complexes of ruthenium were in prospect of catalytic reactions due to the wider scope of oxidation states (from −2 valent to +8) and various coordination geometries in each electron configuration [3]; it was always presented that the catalytic activity and selectivity were different from particular reaction system in light of ligand property, stereo effect and reaction condition, for instance, the complex $RuHCl(PPh_3)_3$ could not only catalyze isomerization reaction, hydrogenation reaction, hydrogen transfer reaction [4] and so on, also was active species for the hydrogenation of the double bond using $RuCl_2(PPh_3)_3$ as the catalyst [5].

Isomerization reaction (Scheme 1) is an example of atom economy in view of green chemistry and one of the most important types of reaction in organometallic chemistry. Alkene isomerization from double bond migration was catalyzed by many transition metal complexes like Fe, Co, Pd, Ru, Ni, Rh, Ti, and so on [6] so far a up to the present, the type of the isomerization from the double migration is generalized as follows: the simply olefin isomerization [7], the diene isomerization [8], the functional isomerization [9] and the isomerization between molecules or in single molecule (including cycloisomerization) [10], and more the reaction can provide a plenty of valuable chemicals [11], such as all kinds of olefin products and their derivatives; in addition it was well applied to organic synthesis [12] for the examples of some terpene difficultly synthesized by the classic functional

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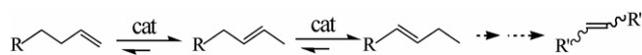
Scheme 1. Catalytic isomerization reaction.

transformation route, and the chiral molecule produced [13]. Which involved in the complexes of Rh, Co, Pd, Ni, Pt, Ru; although there were many catalyst for olefin isomerization now, respectively, there was some shortage to a certain degree: nickel complexes always led olefin to the structure isomerization, the metal (such as cobalt) complexes including carbonyl brought olefin into formylation, and complexes of Pt, Rh, Pd are of lower economy than other like ruthenium complexes for the isomerization in those cases; recently it was reported that ruthenium complexes catalyzed the olefin isomerization [14,15], which were taken into both catalytic efficiency and economy consideration.

The alkene isomerization from terminal to internal is reasonable in thermodynamics. Different mechanisms were proposed for the isomerization process on the basis of different catalytic systems, reaction conditions and experiment phenomena as well as data analyzed, and both main ways were suggested: one was the metal hydride addition–elimination [16] involving the formation and decomposition of an alkyl metal complex and constituting a 1,2-hydrogen migration like 1-pentene isomerization [17] by the complex RuHCl(PPh$_3$)$_3$; the other was π-allyl metal-hydride intermediate [18] connecting with the hydroformylation of olefin with the catalyst, and alkyl metal complex decomposition that resulted in a 1,3-hydrogen shift such as 1-pentene was isomerization [19] by the complex PdCl$_2$(PhCN)$_2$. On the side, other isomerization mechanisms were introduced in the literature to explain the phenomena and results such as the transition metal carbene complex intermediate [20], the dihydrogen π-allyl transition state [21], etc.

In response to the excess surplus for high/low olefin from olefin oligomerization in industry, the only example was the famous SHOP [22], in which the Na/K/Al$_2$O$_3$ or MgO system was used as heterogeneous catalyst to isomerizate high olefin, and it was presented that operation was inconvenience and operating life was short, which could not further meet need for better conversion, no structure isomer and depth which was described as certain degree of the double bond transfer from terminal to internal. Since olefin isomerization plays an important role in both organic synthesis and chemistry industry, we have started an investigation on the isomerization of 1-hexene and 1-octabene by hydride-complexes of ruthenium.

2. Results and discussion

Several hydride-complexes of ruthenium as olefin isomerization catalyst were synthesized according to the earlier reports in the literature: RuH(NO)(PP$_3$)$_3$(I) (**1**), RuHCl(PPh$_3$)$_3$(s)(II) (**2**), RuHCl(CO)(PPh$_3$)$_3$ (II) (**3**), RuH(CH$_3$COO)(PPh$_3$)$_3$(II) (**4**), RuH$_2$(CO)(PPh$_3$)$_3$(II) (**5**). The characteristic absorption peak on Infrared and NMR spectra for the complexes **1**–**5** are listed in Table 1.

It is showed that the characteristic absorption peaks on the Ru–H bond are distinct from the oxidation state of the centre

Table 1
Key band data for hydride-complexes Ru on IR and NMR

Complex code	IR (cm^{-1})	^{1}H NMR	
		δ_{Ru-H} (ppm)	$^2J_{p-H}$ (Hz)
1	ν_{Ru-H}: 1966, ν_{N-O}: 1640	−6.7 (q)	30.4
2	ν_{Ru-H}: 1624	−17.8 (q)	25.6
3	ν_{Ru-H}: 2020, ν_{CO}: 1916, 1900	−18.6 (q)	26.0
4	ν_{Ru-H}: 2013, ν_{COO}: 1526, 1450	−18.7 (q)	28.4
5	ν_{Ru-H}: 1960, 1867, ν_{CO}: 1940	−6.8 (m), −8.3 (m)	15.2, 28.0

metal ruthenium, ligand type and whether to coordinate saturation to the centre atom Ru. The chemical shifts reflecting the electron circumstances for the Ru–H band on NMR spectra were ranked in decreasing order: (**1**), (**5**), (**2**), (**3**), (**4**), and the coupling constants are also distinguished each other, which are beneficial of realizing the isomerization process.

2.1. Influence of temperature on olefin isomerization in the presence of the ruthenium complexes

The data on the catalytic activity of complexes **1**–**5** in temperature are listed in Table 2.

It indicates that the catalyst **1**, **2** are better active than the others for 1-hexene isomerization, and it was found that the two catalysts were instauration in view of coordination in itself, however, on the whole, the conversion of 1-hexene by catalysts above increases in different degree accompanying the temperature on the increase; experiment showed that at certain temperature, the

Table 2
Effect of reaction temperature on 1-hexene conversion by hydride-complexes of Ru

Temperature (°C)	Catalyst code	Composition (%)		
		1-Hexene	2-Hexene	3-Hexene
30	1	39.98	24.83	35.19
	2	42.38	24.13	33.49
	3	95.46	1.83	2.71
	4	98.97	1.03	–
	5	99.64	0.36	–
50	1	38.49	29.97	31.54
	2	40.47	32.67	26.86
	3	92.87	3.93	3.20
	4	98.76	1.24	–
	5	99.46	0.54	–
70	1	31.31	25.27	43.42
	2	32.53	29.93	37.54
	3	91.66	3.99	4.35
	4	80.24	14.78	4.98
	5	95.75	1.49	2.76
90	1	4.46	23.48	72.06
	2	5.60	31.74	62.66
	3	63.05	20.75	16.20
	4	41.96	43.90	14.14
	5	87.86	5.86	6.28

Conditions: catalyst = 2 × 10^{-5} mol; toluene = 1 ml; 1-hexene = 4 ml; t = 30 min; '–': trace.

equilibrium was fast established among 1-hexene, 2-hexene and 3-hexene, and further implied the process of the metal hydride addition–elimination in a sense. As for the catalyst **1**, isomerization of 1-hexene was mentioned in the literature [23], while the cause presenting high activity was investigated for 1-hexene isomerization by the catalyst **2** what follows in the article. In addition, in order to obtain the satisfying conversion, high temperature is necessary for 1-octadence isomerization using the catalysts above in that the reaction is high energy barrier, which was paid attention to and analyzed in the experiment, while by other catalyst of non-hydride-ruthenium complexes, the conversion was terribly low with higher temperature frequently. Unfortunately, the catalyst **1** increasingly became dark the same as the catalyst **3**, **4**, **5** during high temperature reaction, which meant the catalysts inactivation; while the reaction system comprising of **2** all the way kept orange in high temperature bath and presented high thermal stability. So the catalyst **2** was screened to further study.

2.2. Influence of reaction parameters for 1-hexene isomerization by RuHCl(PPh₃)₃(s)

2.2.1. Reaction temperature

The influence of temperature on the catalytic activity of **2** is listed in Table 2.

It is at the relatively lower temperature that isomerization began, the conversion of 1-hexene increases from 57.6% at 303 K up to 94.4% at 363 K all linear isomers of 1-hexene were produced, which is 2-hexene, 3-hexene, and other product wasn't detected, and their amount goes up close two times when the temperature was raised from 303 to 363 K. It is presented that the reaction process is easily adjusted by the catalyst **2** in thermodynamic energy:
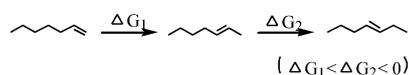
So, in that case the low temperature may be taken into consideration.

2.2.2. Reaction time

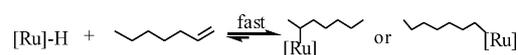The result of reaction time is obtained to see Table 3.

At 50 °C the conversion of 1-hexene increases from 59.5% to 63.04% when reaction time increases from 30 to 180 min, which yield does not rise obviously, and it demonstrates that

the catalytic reaction is fast dynamitic process and establishes equilibrium in shorter time:

And in the other, at 120 °C, the conversion of 1-hexene accompanying the time from 30 to 180 min is fundamentally kept stable within the error for the gas chorography (Table 4), exactly, within 1 h the equilibrium has been established to a certain degree, but the products analyzed by ^{1}H NMR showed that the transformation between *cis*- and *trans*-isomer still existed which directed the *cis*-isomer, the result is the same as the literature [24] reported previously:

trans-2-hexene $\rightleftharpoons$ *cis*-2-hexene,

trans-3-hexene $\rightleftharpoons$ *cis*-3-hexene
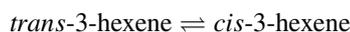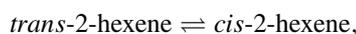
And more, the data above is confirmed according to the integrated equation [14]: $kt = \ln[a_0/a_0(1-x)]$ (a_0: the initial concentration of 1-hexene, t: the reaction time, x: the percentage conversion); by calculation, the first-order reaction average rate $\bar{k}$ is 3.0×10^{-2} m^{-1}. In brief, the reaction time is freely chosen in a certain temperature condition.

2.2.3. Effect catalyst concentration

This aspect of catalyst concentration (in toluene) or the catalyst number (constant solvent amount) is reported in Table 5.

The conversion of 1-hexene rises from 26.97% to 59.75% which only increases more two times when the catalyst amount in 1 ml toluene is increased from 1.0 to 15.0 mg which increases 15 times, and it was finally found that the catalyst solubility became worse at a temperature if the catalyst amount was added more; the result is satisfying when the ratio of the hexene to the catalyst is 2000, which is selected for further research. In

Table 4
Effect of reaction time on 1-hexene conversion by RuHCl(PPh₃)₃(s) (120 °C)

Time (h)	Composition (%)		
	1-Hexene	2-Hexene	3-Hexene
1.0	2.67	20.53	76.80
2.0	2.64	20.78	76.58
4.0	2.52	20.24	77.24
7.0	2.50	20.05	77.45
11.0	2.46	19.64	77.90

Conditions: catalyst = 2×10^{-5} mol; toluene = 1 ml; 1-hexene = 4 ml; $T = 120$ °C.

Table 3
Effect of reaction time on 1-hexene conversion by RuHCl(PPh₃)₃(s) (50 °C)

Time (min)	Composition (%)		
	1-Hexene	2-Hexene	3-Hexene
30	40.47	32.67	26.86
60	40.25	33.63	26.13
90	40.14	33.29	26.57
120	39.91	32.57	27.52
180	39.86	32.55	27.59

Conditions: catalyst = 2×10^{-5} mol; toluene = 1 ml; 1-hexene = 4 ml; $T = 50$ °C.

Table 5
Effect of catalyst number on 1-hexene conversion by RuHCl(PPh₃)₃(s)

Catalyst amount (mg)	Composition (%)		
	1-Hexene	2-Hexene	3-Hexene
1.0	90.69	5.03	4.28
5.0	83.14	9.32	7.54
10.0	60.48	22.74	16.78
15.0	53.92	25.45	20.63
20.0	49.98	27.61	22.41

Conditions: time = 30 min; toluene = 1 ml; 1-hexene = 4 ml; $T = 50$ °C.

Table 6
Results of recycling on 1-hexene conversion by RuHCl(PPh$_3$)$_3$(s)

Circling	Composition (%)		
	1-Hexene	2-Hexene	3-Hexene
1	42.28	24.18	33.54
2	40.91	37.60	21.49
3	40.87	32.87	26.26
4	42.66	33.27	24.07
5	51.27	28.31	20.42
6	51.33	28.17	20.50
7	60.52	24.57	14.91

Conditions: catalyst $= 2 \times 10^{-5}$ mol; toluene $= 1$ ml; 1-hexene $= 4$ ml added for every time; $t = 30$ min; $T = 50\,^\circ$C.

addition, the conversion decreased a little when the catalyst contained some free triphenyl phosphorus in the experiment, which demonstrated the competing coordination to the centre Ru between olefin and PPh$_3$ in catalytic process.

2.2.4. Recycling test

The work is usually used to check the catalyst operating life.

Table 6 presents the result of every successive recycle. During the beginning four times recycle, it is presented that the conversion of 1-hexene is almost the same, and that it's activity was kept; the data decreases to a little degree after the fifth and sixth recycle, thereafter the activity declines to a lager degree, the causes are as follows: (1) the catalyst color began to change from red-violet to thin dark-red, and hinted the Ru–H bond in catalyst was reduced in a sense, which was confirmed by ^{1}H NMR; (2) the catalyst was lost, that is, one was that the catalyst was adsorbed by the reactor without in the solvent, the other was that it was taken away with solvent during the operation of the evacuation.

2.3. 1-Octadecene isomerization by RuHCl(PPh$_3$)$_3$(s)

The feature that the complex RuHCl(PPh$_3$)$_3$(s) catalyzed 1-octadecene isomerization lies in: high activity, thermal stability and the solvent-free system. At 180 $^\circ$C, equilibrium conversion of 1-octadecene got to above 94.60% when the ratio of the catalyst to the substrate was 1:200, the GC spectrum (Fig. 1) shows one of the isomerization results. In experiment, the process is thought:
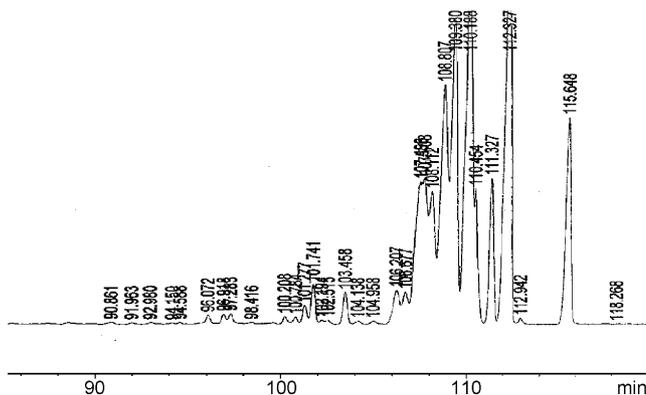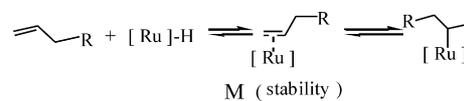

Fig. 1. GC Spectrum of 1-octadecene isomerized.

That is obviously different from 1-hexene isomerization: the system color kept the orange during the reaction, the analysis by ^{1}H NMR did not show the peak of the Ru–H bond which probably the catalyst concentration containing the Ru–H bond was too low, but in theory M is stability. While for 1-hexene, the red-violet color doesn't change all the time, and ^{1}H NMR spectra could reflect the Ru–H bond, and uncovered that 1-hexene isomerization is fast process from other side.

2.4. Generalization in performance on olefin isomerization by hydride-complex of Ru

The generalization deriving from experiments observed and results analyzed is described below:

(1) It is a key step whether olefin effectively coordinates with transition metal complex or not for the reaction to be happened.
(2) For a complex, the [Ru]–H activity on isomerization is closely related to ligands such as category, property, stereo structure.
(3) The olefin structure as the reaction substrate influences reaction process and equilibrium state to a different degree.

2.5. Primary discussion on mechanism

The results have presented activity and efficiency on isomerization by **2**; some causes were investigated: the first-order reaction rate is listed in Table 7 which also contains the same reaction catalyzed by RuHCl(PPh$_3$)$_3$(s) which was synthesized in different method [25,26] early reported and in which the only difference lies in s (solvent) adsorbed by catalyst, obviously the catalytic result is here better than ones recorded in previous work.

Taken into solvent effect consideration, the same result was acquired when benzene only replaced commensurate toluene as a solvent on the comparable condition, and thought about potential species RuH$_2$(PPh$_3$)$_3$ produced in situ, the poor result was led to on the identical condition when the RuH$_2$(PPh$_3$)$_3$ [24] was used as olefin isomerization catalyst yet; what's more, the conversion what little rose but was not so conspicuous when EtOH was added to the reaction system successively; furthermore, to

Table 7
The different rate from RuHCl(PPh$_3$)$_3$(s) by different synthesis method for 1-hexene isomerization

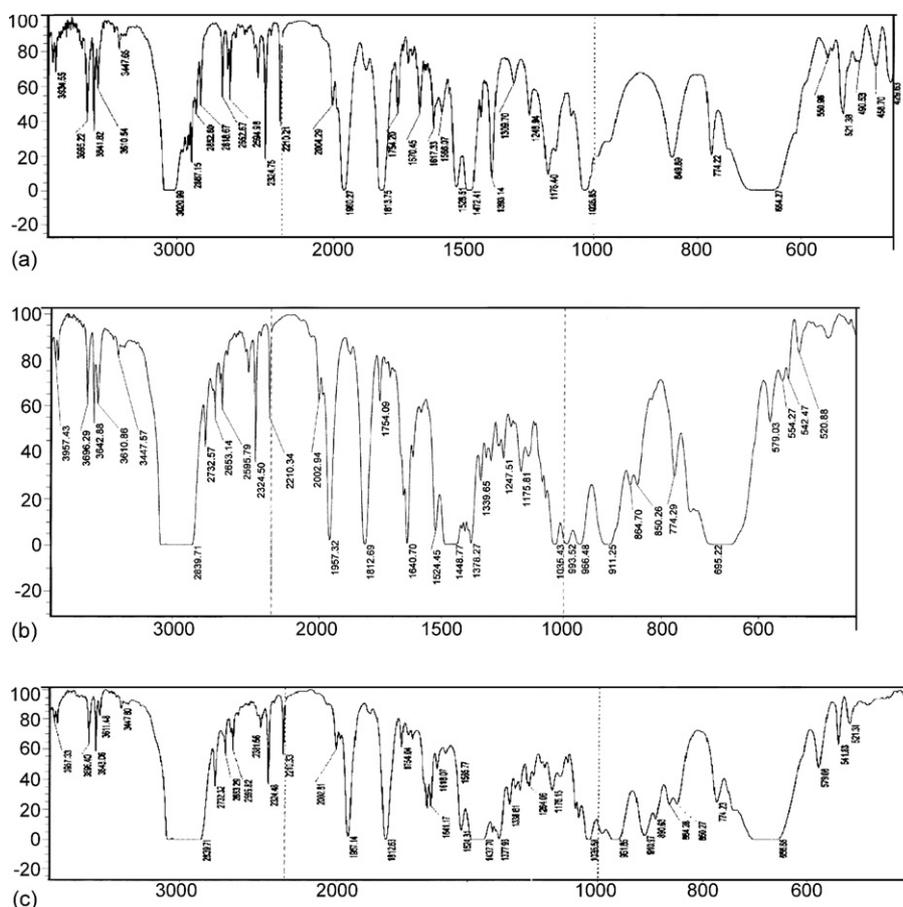| Catalyst	s (in synthesis)	Substrate, s (in catalysis)	Rate (min^{-1})
RuHCl(PPh$_3$)$_3$	⬡	1-hexene ⬡	Non
	⬡ and EtOH	1-hexene ⬡	$<3 \times 10^{-4}$ (in H$_2$)
	EtOH	1-hexene ⬡	3.0×10^{-2}

s: solvent.

Fig. 2.

check tracking experiment done by IR, it showed that the absorption peaks on EtOH were C–O absorption state (Fig. 2(a))) at 1025–1040 cm^{-1} when the system only had catalyst and solvent, while the ones were changed (Fig. 2(b) and (c)) at 0.5 and 1.0 h, respectively, after 1-hexene was added to; otherwise, the anagogic structure (A or/and B [27]) (Fig. 3) as a transition state possibly influenced the process, unfortunately the reaction system could not be probed.

In general, it is supposed ligand exchange which presents olefin in place of EtOH adsorbed by RuHCl(PPh$_3$)$_3$ is responsible for the reaction to start fast, and the terminal olefin isomerization is feasible in thermodynamic, which can interpret the
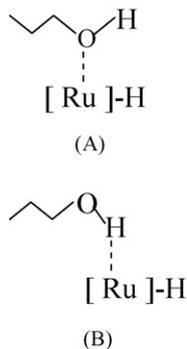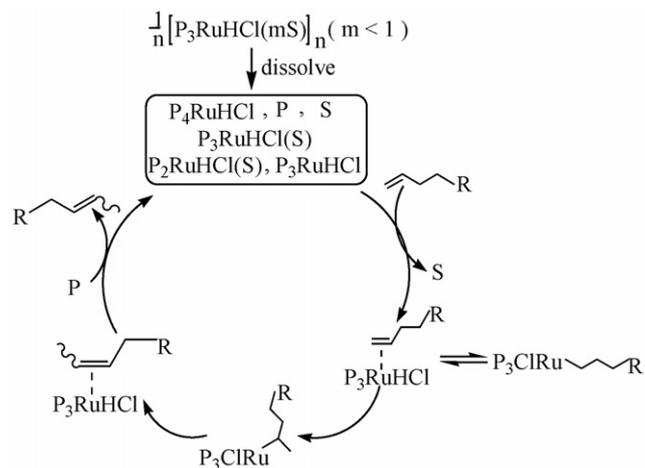

(A)

(B)

Fig. 3.

Scheme 2. Mechanism of RuHCl(PPh$_3$)$_3$(s)-catalyzed olefin isomerization.

difference from the same catalyst but the distinguished synthesis method. And being connected with the associated catalytic performance reported in previous literature [28,29], the below mechanism proposed (Scheme 2).

3. Conclusion

(1) Being taken insert–elimination process of olefin isomerization into account, several complexes containing the

Ru–H bond were synthesized according to previous work: RuH(NO)(PPh$_3$)$_3$, RuHCl(PPh$_3$)$_3$(s), RuHCl(CO)(PPh$_3$)$_3$, RuH(CH$_3$COO)(PPh$_3$)$_3$ and RuH$_2$(CO)(PPh$_3$)$_3$, and the complex of RuHCl(PPh$_3$)$_3$(s) was screened for further investigation on the base of activity and life-operating on isomerization of 1-hexene and 1-octadecene.

(2) The influence of temperature, reaction time, catalyst concentration on 1-hexene isomerization by RuHCl(PPh$_3$)$_3$(s) was studied, at 50 °C, 150 mg catalyst (in 1 ml toluene), 180 min, the 63.04% conversion of 1-hexene was attained, and in accordance with other condition, at 120 °C that reached 97.54%, further the *cis*-isomer rose with the reaction time increasing and indicated the better life-operating in the light of catalytic cycle.

(3) The 1-octadecene isomerization by RuHCl(PPh$_3$)$_3$(s) presented high activity, thermal stability and the solvent-free system, at 180 °C the equilibrium conversion of 1-octadecene reached above 94.6% with the condition of the 1:200 ratio of catalyst to substrate.

(4) Obvious difference was presented on the isomerization by RuHCl(PPh$_3$)$_3$(s) for 1-hexene and 1-octadecene: (i) on temperature for isomerization conversion: the reaction temperature was more higher in 1-octadecene than in 1-hexene, and more, at lower temperature, 1-octadecene process hardly proceeded; (ii) on solvent for the isomerization reaction: the system on 1-hexene was necessary for solvent such as toluene, benzene, while one on 1-octadecene was without solvent, and at room temperature the catalyst may better dissolve 1-octadecene; (iii) on intermediate: by ^{1}H NMR spectra, the certain intermediate on 1-octadcene isomerization was relatively stable, while that was rather reactive in hexene, which the quick reaction process was interpreted.

(5) Evidence on isomerization of 1-hexene and 1-octadecene by RuHCl(PPh$_3$)$_3$(s) provided to recognize the specific process: the catalytic property was closely relation with coordination circumference of the centre metal, ligand property and substrate.

(6) The mechanism was carefully studied; the solvent adsorbed by the catalyst should be responsible for high activity and efficiency.

4. Experimental

4.1. Materials

Methanol and ethanol were distilled after refluxing over the corresponding magnesium alkoxides under nitrogen atmosphere, triphenyl phosphine recrystallized from purified ethanol, *n*-hexane and toluene distilled after refluxing with sodium thread adding a bit biphenyl ketone under the same nitrogen atmosphere, 1-hexene and water were refluxing for a long time with nitrogen stream, 1-octadcene (purity: 90%) was degassed by the replacement of nitrogen under reduced pressure for three times in froze ethanol bath, sodium acetate was dried with heat for a long time under reduced pressure, Ruthenium trichlorohydrate and sodium borohydride were dealt with nitrogen to remove oxygen before use.

4.2. Preparation of catalysts

Generally considered, experiment, unless otherwise specified, was operated under a nitrogen atmosphere using the Schlenk technique.

RuHCl(PPh$_3$)$_3$(s):RuCl$_2$(PPh$_3$)$_3$ (1.91611 g, 2.0 mmo1) and KOH (0.1120 g, 2.0 mmo1) were placed in a 100 ml Schlenk flask and purged with nitrogen, dry EtOH (40 ml) was added by syringe, the brick red suspension system was stirred, and then carefully slowly heated till 100 °C (bath temperature) to reflux under nitrogen, and during the process, the system color became from brick red to khaki till purple, the reaction was kept stirring and refluxing for about 2 h, thereafter the solution was allowed to coo1 to room temperature, the purple precipitate was collected in core filter purged by nitrogen, and did filter-pressing using nitrogen, washed methanol (2 ml × 10 ml) water oxygen-free (5 ml), and again with methanol and *n*-hexane (5 ml × 5 ml), then pressed filter to close dry, and dried in vacuum over silica gel for a long time the purple powder solid (1.7 g, 91.9%).

Other complexes were prepared according to the previous literature their spectroscopic characteristics were in agreement with the data reported: RuH(NO)(PPh$_3$)$_3$ [30], RuHCl(CO)(PPh$_3$)$_3$ [31], RuH(CH$_3$COO)(PPh$_3$)$_3$ [32], RuH$_2$(CO)(PPh$_3$)$_3$ [33].

4.3. Procedures

The isomerization reaction of olefin was carried out in a 25 ml stainless autoclave with magnetic stirrer, or for 1-octadecene isomerization was also done in three bottle flask, the autoclave with weighted catalyst was sealed and displaced with nitrogen for three times, unsealed and then past through with the nitrogen stream, other reaction substrate and necessary solvent was added in by syringe, and sealed again, finally the autoclave was put into a constant bath, and heated to the desired temperature; after the expiration of the desired reaction time, the autoclave was taken out and cooled to room temperature naturally, and hexene mixture was slow distilled and collected, while octadecene mixture was distilled under reduced pressure with heat.

4.4. Measurement and analysis

The complexes above were characterized by infrared spectra measured on the neat condition in a Nicolet 50X FT-IR spectrophotometer and ^{1}H NMR spectra recorded By a Varian/Nova-400 type spectrometer at 400 MHz, the chemical shifts were determined in ppm using TMS as internal standard, quantitative analyses of the reaction products were performed by a SRI8610C type gas-chromatograph (length: 60 m), the correcting factors were introduced in consideration of the isomerization process to be discussed.

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