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Olefin isomerization reactions catalyzed by ruthenium hydrides bearing Schiff base ligands

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A series of *in situ*-generated ruthenium hydride complexes $Ru(PPh_3)_2(CO)H(L^n)$ ($n = a-h$) incorporating a Schiff base ligand was investigated for the isomerization of olefins. ^1H-NMR was used to characterize the new hydride species in combination with ^{31}P-NMR. Allylbenzene and 1-octene were used as model substrates. Temperature, solvents and catalyst/substrate mole ratio were taken into account as parameters to optimize the isomerization reaction. All catalysts showed the best performance in 2-butanol, suggesting that the catalytic activity depends not only strongly on the steric and electronic environment of the ruthenium but also on the chosen solvent. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: isomerization; ruthenium hydride; organometallic compounds; Schiff base

Introduction

Since all kinds of unsaturated hydrocarbons play an important role in organic synthesis, the isomerization of double/triple bonds has been one of the highlights of transition-metal-catalyzed synthesis in terms of both academic curiosity and industrial interests.[1] Certain transition metal complexes based on Fe,[2–4] Pd,[2,3] Rh,[4] Pt,[5] Ni,[3,6] Ir,[7] Ru,[8–11] and Cr[12,13] are known as catalysts for isomerization. For instance, the Wilkinson catalyst $(PPh_3)_3RhCl$ is frequently employed in the isomerization of allylic ethers.[14]

Ruthenium hydride has been applied as a catalyst for the olefin isomerization[11,15–20] since Ewing *et al*. reported on the double bond migration of 1-pentene to give *cis*-2-pentene (60%) and *trans*-2-pentene (40%) making use of $RuHCl(PPh_3)_3$.[21] Although many elegant applications corroborate the idea that ruthenium hydride complexes may perform isomerization in a more conventional approach,[24–29] in most cases they only exist as intermediate species. Furthermore, the instability of the hydride retards the application of this kind of catalyst. In order to discover an effective catalyst applicable under mild conditions, variation of the ligand environment is expected to tune the stability, the reactivity and even the selectivity of those compounds.

As all the properties of the catalysts are dictated primarily by the coordination environment around the metal center, complexation of transition metal compounds with specific ligands is of significant importance for the catalytic activity. In addition, Schiff bases bearing transition metal complexes offer a powerful synthetic methodology for organic transformations. In particular, they play a crucial role in ligand optimization strategies, resulting in a novel class of robust and active ruthenium catalysts.[22–27] By the proper choice of the substituents on the Schiff base, the desired physical and chemical properties could be induced into the prepared complexes.

Although Schiff base ruthenium hydride complexes have been reported for several decades,[28,29] study of their isomerization activity remains relatively scarce. Their antibacterial activities and oxidation activities in alcohols have been widely investigated..[30–32] With the intention of developing long-lived, highly active ruthenium isomerization catalysts, we explored the substitution of tertiary phosphines by Schiff bases *in situ* from ruthenium hydride compounds to afford an extensive range of ruthenium complexes that would subsequently show improved catalytic activities and stabilities for isomerization compared with their parent compound, $RuH_2(CO)(PPh_3)_3$.

Experimental

General

Unless otherwise stated, all reactions were carried out under a dry argon atmosphere following conventional Schlenk techniques and all solvents were distilled from the appropriate drying agents and deoxygenated prior to use. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian 300 spectrometer in $CDCl_3$ (δ, ppm). The salicylaldehydes and aromatic amines to synthesize the Schiff Base ligands and $RuCl_3{\cdot}nH_2O$ to synthesize the precursor were all purchased from Aldrich and used as received. The precursor $RuH_2(CO)(PPh_3)_3$ was prepared according to the literature.[33] All other chemicals used were of analytical grade without further purification.

Yields and selectivities were obtained using a Finnigan Trace GC Ultra with an Ultra Fast Column Module (PH-5 5% diphenyl–95% dimethyl poly-siloxane capillary, helium carrier gas, 1 ml/min),

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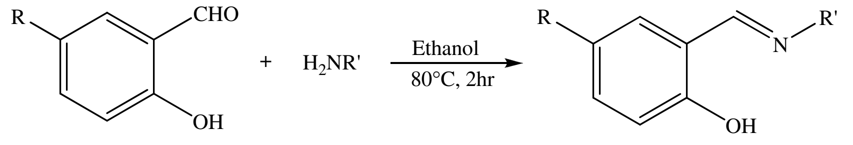
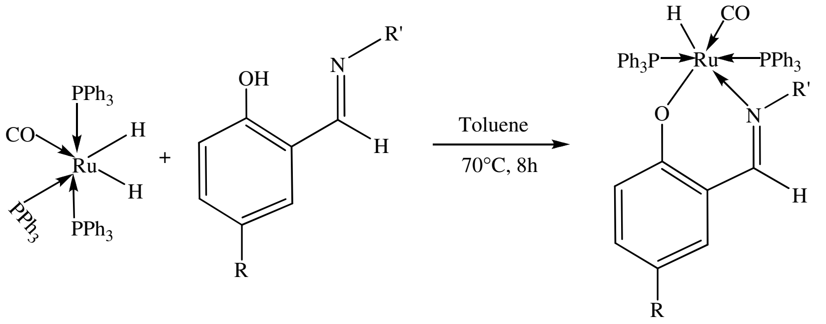


R = H R'= 2-Me-phenyl (a) R = NO_2 R'= 2-Me-phenyl (e)
R = H R'= 4-tBu-phenyl (b) R = NO_2 R'= 4-tBu-phenyl (f)
R = H R'= 2,6-dimethylphenyl (c) R = NO_2 R'= 2,6-dimethylphenyl (g)
R = H R'= 4-bromo-2,6-dimethylphenyl (d) R = NO_2 R'= 4-bromo-2,6-dimethylphenyl (h)

Scheme 1. Synthesis of Schiff bases.



R = H R'= 2-Me-phenyl (1) R = NO_2 R'= 2-Me-phenyl (5)
R = H R'= 4-tBu-phenyl (2) R = NO_2 R'= 4-tBu-phenyl (6)
R = H R'= 2,6-dimethylphenyl (3) R = NO_2 R'= 2,6-dimethylphenyl (7)
R = H R'= 4-bromo-2,6-dimethylphenyl (4) R = NO_2 R'= 4-bromo-2,6-dimethylphenyl (8)

Scheme 2. Synthesis of the ruthenium hydride Schiff base catalysts **1–8**.

column (10 m × 0.10 mm, 0.40 µm) and an FID = Flame Ionization Detector detection system. The temperature program started at 50 °C and heated at 20 °C/min up to 255 °C.

Pretreatment of the substrates was necessary before starting the isomerization reaction. 1-Octene was passed through a column of neutral alumina (Acros, 50–200 µm), containing 15 g of alumina per 100 ml of 1-octene, into a Schlenk flask; then, 1-octene was deoxygenated. In an empty 15 ml reaction vessel, an appropriate quantity of the catalyst under investigation and solvent was transferred under a constant Ar flow. Then the substrate was added and the vessel was immersed in an oil bath, allowing equilibration to the desired temperature before timing.

Prior to GC-analysis, the reaction mixture was purified over a silica filter in order to remove the catalyst. Hexane was used as solvent to prepare the GC samples and 1-dodecane was added as internal standard.

Preparation of Schiff Base Ligand

The Schiff bases were prepared using conventional methods.[34] The resultant crude products were isolated as yellow solids and purified by washing with cold pentane followed by drying *in vacuo*, affording salicylaldimines in quantitative yields. The spectroscopic properties[35] of the synthesized Schiff bases, see Scheme 1, are in agreement with the literature data.[34]

Preparation of Ruthenium Hydride Precursor

The precursor $RuH_2(CO)(PPh_3)_3$ was prepared according to the literature and the characterization was in good agreement with the literature data.[33]

Preparation of Schiff Base Ruthenium Hydride Complexes

The new hexa-coordinated ruthenium (II) complexes of the type $RuH(CO)(PPh_3)_2(L^n)$ (L = Schiff base ligand, n = **a**–**h**) were prepared according the reaction depicted in Scheme 2. To a toluene solution of the bidentate salicylaldimine ligand **a**–**h** (1.1 equiv.) was added drop-wise a toluene solution of $RuH_2(CO)(PPh_3)_3$ (1 equiv.). After addition, the mixture was heated to 65–80 °C for about 5 h to afford a pale yellow solution. The new species were evidenced by ^1H and ^{31}P NMR and yields between 50 and 90%, based on ^{31}P NMR measurements, were obtained. ^1H and ^{31}P NMR also confirmed that the starting hydride compound was no longer present.

Results and Discussion

Synthesis and Characterization

Since ruthenium hydrides were found to be active catalysts for isomerization, a series of ruthenium hydride Schiff base complexes $RuH(PPh_3)_2(CO)(L^n)$ (with n = **a**–**h**) were developed. Compound **1** was reported by Vart A, *et al.*, although without any further exploration of application.[28]

Based on the NMR data given in Table 1, the stereochemical structure of compounds **1**–**8** was in agreement with the general structure depicted in Scheme 2. From the ^1H NMR data [^1H, δ_{RuH} ca. −10 ppm, $^2J(PH)$ ca. 20–22 Hz, $^4J(HH)$ ca. 2 Hz], especially, the coupling $^4J(HH')$ between hydridic and azomethine (–N=CH–) protons favors the structure between the alternative arrangements with the hydride *trans* to the O-donor site. The ^{31}P NMR resonances [$^{31}P\{^1H\}$, δ_{PPH3}, ca. 38.9–43.0 ppm (s)] were found to be singlets,

Table 1. The ^{1}H and ^{31}P NMR data of $RuH_2(CO)(PPh_3)_3$ and **1**–**8**

	^{1}H (ppm)	^{31}P(ppm)
$RuH_2(CO)(PPh_3)_3$	−6.885(t), −8.905(m)	58.245(d), 45.732(t)
1	−11.336(t)	38.936(s)
2	−10.931(t)	41.273(s)
3	−16.394(t)	40.213(s)
4	−14.364(t)	38.075(s)
5	−11.263(t)	38.940(s)
6	−10.891(t)	41.657(s)
7	−16.748(t)	40.205(s)
8	−14.534(t)	39.926(s)

because for bulky phosphines, e.g. PPh_3, no effective coupling was observed between the two phosphine ligands ($^{31}P-^{31}P$).[36] Furthermore, these observations indicate that the phosphine ligands are orientated *trans* to each other. The Schiff base ligands coordinate in a bidentate fashion with the N,O donors forming a six-membered chelating ring.[10,11,22–27] All above observations support the general structure depicted in Scheme 2.

The respective ^{1}H resonances relative to the hydride in complexes **1**–**8** were strongly shifted downfield or upfield (−10.9 to −16.7 ppm), depending on the electronic properties of the R′-group on the Schiff base.

Furthermore, a number of features of Schiff base ligands make them attractive for catalytic applications, particularly the decreased liability and/or higher stability in comparison to the precursor compound. For complexes **1**–**8**, no changes were found in the NMR spectrum after several days, even in open air. In addition, the new compounds are more stable than most of the reported ruthenium hydrides, which degrade in less than 24 h in air.

Isomerization Activities

Since hydride complexes have been corroborated in the literature as isomerization catalysts,[37–41] by applying different R or R′ groups in the Schiff base ligand, the influence of electronic and steric factors of the ligand in the ruthenium hydride complexes was the subject of this study. To elucidate the source of the activity differences and establish relative stabilities of the various complexes, the reactivities of the ruthenium hydrides **1**–**8** were examined using 1-octene and allylbenzene as model substrates.

Complexes **1**–**8** were treated with an excess of 1-octene at different temperatures (60, 80 and 100 °C) for 12 h and the activities were investigated. The results are summarized in Tables 2–4. To compare and optimize their activities, different catalyst–substrate ratios (1 : 1000, 1 : 5000 and 1 : 10000) and different solvents were applied.

During the isomerization reaction, three products were generated – 2-octene, 3-octene and 4-octene – indicating that **1**–**8** catalyzed the isomerization of 1-octene. Initial GC and NMR results proved that neither metathesis nor dimerization took place.

Each of the new species, **1**–**8**, were superior to $RuH_2(CO)(PPh_3)_3$ under the experimental conditions described in Table 2. High conversions were mostly achieved by the new complexes. Moreover, the increased activity of these catalysts was not accompanied by a decrease in stability towards towards air and moisture. This observation results from the contribution of the Schiff base ligand. Two donor atoms, N and O, in the coordinated Schiff base exert opposite electronic effects: the phenolate oxygen is a hard donor stabilizing the higher oxidation state of the ruthenium whereas the imine nitrogen is a softer donor and, consequently, will better stabilize the lower oxidation state of the ruthenium atom. In this way a flexible interaction between these two binding sites can be achieved.

It follows from Table 2 that a higher catalyst loading results in a higher substrate conversion. However, the variance is not linear and some differences in conversion are less than 1%, i.e. there are no significant differences between these two mole ratios (1 : 1000 to 1 : 5000). Since a lower catalyst loading is much more attractive in comparison to other reported catalysts, this is a noteworthy improvement.[42–44]

The temperature has a drastic influence on the activity; increasing the temperature did not lead to increased conversion. A higher temperature promoted the decomposition of the catalyst, resulting in a lower yield. Complexes **1, 2** and **5**–**7** performed best at 80 °C, while complexes **3** and **4** needed 100 °C to complete the isomerization reaction. Only complex **8** showed excellent performance at 60 °C.

The conversion of 1-octene in the presence of $RuH_2(CO)(PPh_3)_3$ and complexes **1**–**8** without solvent is depicted in Fig. 1. Except for complexes **1** and **2**, all complexes achieved over 95% conversion. Using complex **8**, a conversion of 98.1% was reached, and complexes **3, 4** and **6**–**8** reached >95% conversion within the first half-hour. Complexes **1, 2** and **5** showed a much slower rate of reaction. All nitro-containing complexes displayed a higher activity compared with the non-nitro-containing compounds.

As discussed above, it seems that, after adjusting the steric and electronic effects around the ruthenium center through an appropriate selection of the substituents on the Schiff base unit, the activity of ruthenium hydride complexes depended on the R′-group of the Schiff base. The experimental data suggest that the electronic influence of the Schiff base has a greater impact on the catalytic performance than the steric bulk of the Schiff base.

Based on the results discussed above, most of the catalysts demonstrated an excellent performance at a catalyst–substrate mole ratio of 1 : 1000. The same ratio was used to study the influence of the solvent.

Comparing the percentage conversion of 1-octene depicted in Table 3, it can be seen that the various solvents affected the isomerization in different ways. 2-Butanol was the unique solvent for all catalysts. For the other solvents, it was difficult to observe a general trend. Moreover, the solvent effect on this series of catalysts was not affected by the temperature.

Because of the distinct thermal stability in different solvents, the best performance of the catalyst did not always appear at higher temperatures. The same catalyst could generate higher yields at a different temperatures depending on the solvent. For instance, catalyst **1** gave 97.4 and 95.2% yields in $CHCl_3$ and $CH_3CHClCH_2Cl$, respectively, at 60 °C, while in methanol and 2-butanol, the highest yields obtained at 80 °C were, respectively, 87.2 and 95.9%. This phenomenon appears to be true for all catalysts. Furthermore, it seems that the solvent effect improved the activity of catalysts containing a small substituent on the Schiff base (**1** and **5**).

Using allylbenzene as substrate, 2-butanol was still the solvent of choice since all the catalysts were promoted. Varying the solvent resulted in a significant change in conversion, e.g. for catalyst **1** a conversion of 32.3% was obtained in $CH_3CHClCH_2Cl$ at 60 °C, while when using 2-butanol a conversion of 86.6% was reached at 60 °C. For catalyst **7**, at all temperatures high conversions were obtained when $CHCl_3$ or 2-butanol was used as the solvent. For catalyst **6**,

Table 2. 1-Octene conversion by $RuH_2(CO)(PPh_3)_3$ (precursor) and **1**–**8**, without solvent

Temperature (°C)	Precursor	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
C : S[a] *ratio 1 : 1000*									
60	42.0	62.5	90.6	96.9	95.2	89.6	97.1	95.7	98.1
80	86.5	96.1	96.6	96.3	97.3	97.4	97.4	97.4	97.4
100	88.7	94.8	96.5	97.5	97.4	97.3	97.4	96.9	97.4
C : S[a] *ratio 1 : 5000*									
60	36.0	39.6	86.4	71.4	93.2	73.1	96.7	60.2	96.6
80	40.4	87.6	96.5	91.5	97.0	97.3	96.2	92.1	96.7
100	60.3	92.3	94.6	94.9	96.8	97.2	97.1	95.6	97.2
C : S[a] *ratio 1 : 10 000*									
60	1.8	32.9	20.4	10.3	20.3	42.6	89.4	24.7	89.9
80	19.1	26.2	87.0	35.9	84.0	91.2	91.2	85.9	96.1
100	40.3	81.7	92.7	86.2	94.3	92.3	96.9	95.6	97.2

[a] C : S ratio, catalyst/substrate mole ratio.

Table 3. Percentage conversion for the isomerization of 1-octene by complexes **1**–**8** with solvent

	Solvent					
Temperature (°C)	No solvent	$CHCl_3$	$CH_3CHClCH_2Cl$	MeOH	2-Butanol	Toluene
Catalyst 1						
60	62.5	92.2	95.2	37.9	92.1	92.1
80	96.1	96.7	91.0	87.2	95.9	96.4
100	94.8	97.0	92.9	60.8	94.0	96.9
Catalyst 2						
60	90.6	65.1	57.7	96.1	93.2	50.2
80	96.6	58.0	74.0	89.8	89.5	66.4
100	96.5	83.0	74.0	94.0	95.3	61.7
Catalyst 3						
60	96.9	95.8	72.5	52.0	97.8	38.3
80	96.3	92.3	88.5	65.8	96.5	54.4
100	97.5	96.3	77.8	76.0	96.3	75.3
Catalyst 4						
60	95.2	89.9	75.1	97.2	90.8	15.8
80	97.3	98.0	77.9	97.7	95.5	17.0
100	97.4	98.8	80.8	95.7	96.6	36.4
Catalyst 5						
60	89.6	71.3	59.2	45.1	94.1	72.5
80	97.4	88.4	67.7	62.6	98.6	86.8
100	97.3	84.0	59.3	63.7	96.4	90.6
Catalyst 6						
60	97.1	93.2	85.5	56.3	96.2	69.3
80	97.4	93.2	96.0	63.2	96.7	75.0
100	97.4	94.4	96.3	60.3	97.1	85.8
Catalyst 7						
60	95.7	77.5	53.3	91.1	87.4	57.9
80	97.4	74.8	54.3	95.5	87.9	61.3
100	96.9	75.6	66.3	96.4	94.5	60.9
Catalyst 8						
60	98.1	91.0	71.2	43.9	96.2	63.9
80	97.4	91.0	59.9	33.3	96.6	76.3
100	97.4	100.0	68.9	19.5	95.8	76.9

Table 4. Percentage conversion for the isomerization of allylbenzene by complexes **1**–**8** with solvent

Temperature (°C)	Solvent $CHCl_3$	$CH_3CHClCH_2Cl$	MeOH	2-Butanol	Toluene
Catalyst 1					
60	33.4	32.3	56.7	86.6	50.7
80	27.6	62.5	69.7	97.6	75.6
100	61.2	50.2	76.3	93.0	84.6
Catalyst 2					
60	12.8	15.3	69.1	99.8	10.9
80	17.4	45.9	53.1	97.8	15.4
100	37.2	65.1	48.6	99.7	18.8
Catalyst 3					
60	99.7	57.9	95.5	98.4	18.2
80	99.9	58.1	95.7	99.7	29.8
100	96.4	59.2	92.1	99.6	34.1
Catalyst 4					
60	81.5	82.5	21.7	99.4	15.0
80	96.6	97.2	51.2	99.7	35.7
100	95.2	99.7	76.7	99.8	26.8
Catalyst 5					
60	26.0	23.4	80.1	90.9	10.6
80	56.8	45.4	85.2	99.8	71.4
100	52.9	66.2	95.9	99.4	82.9
Catalyst 6					
60	49.3	46.9	15.6	99.8	30.8
80	40.3	75.3	18.7	99.9	57.1
100	64.1	70.6	13.2	99.9	72.2
Catalyst 7					
60	92.6	47.8	98.9	77.0	14.0
80	92.9	53.0	94.9	65.2	20.9
100	92.5	50.6	99.2	79.3	27.4
Catalyst 8					
60	95.7	9.6	59.0	75.7	9.8
80	94.0	17.7	47.1	85.5	39.1
100	89.9	43.8	73.8	96.2	34.9

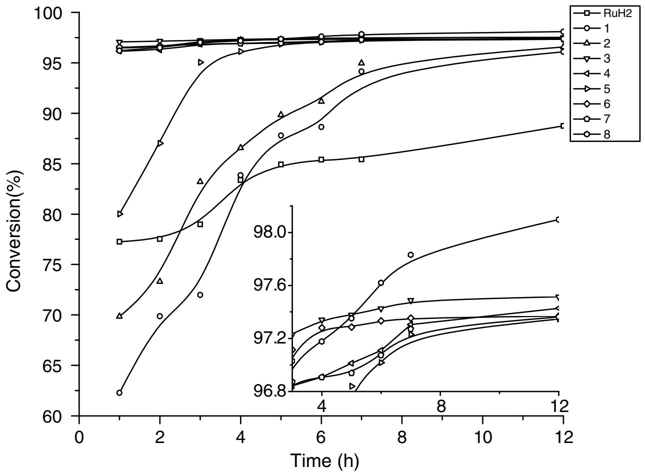


Figure 1. Isomerization results of 1-octene using $RuH_2(CO)(PPh_3)_3$ ($=RuH_2$) and complexes **1**–**8** (without solvent, temperature 80 °C, C : S ratio 1 : 1000).

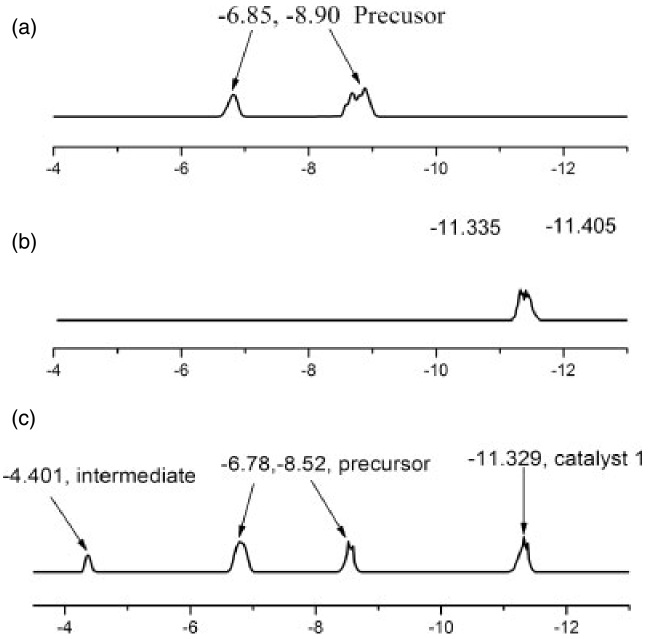


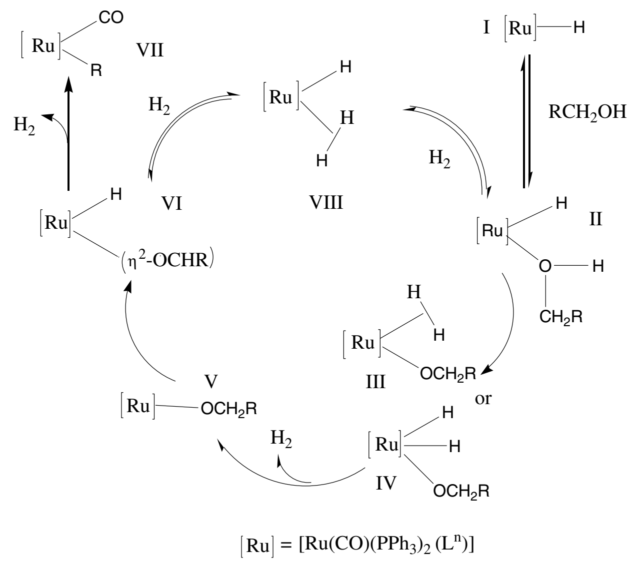
Figure 2. Hydride region of the ^{1}HNMR spectrum of (a) precursor–$RuH_2(CO)(PPh_3)_3$, (b) catalyst **1**–$RuH(CO)(PPh_3)_2$ (**L^a**) and (c) intermediate, catalyst **1**-$RuH(CO)(PPh_3)_2$ (**L^a**) and precursor–$RuH_2(CO)(PPh_3)_3$.

the solvent of choice was 2-butanol; at 60 °C full conversion was achieved. In general, it can be concluded that 2-butanol is the preferred solvent for this series of ruthenium Schiff Base hydrides.

Because many hydride complexes, such as $RuH_4(PPh_3)_3$ and $RuH(BH_4)(PMe_2Ph)_3$, are able to decarbonylate alcohols, it was expected that this decarbonylation would also occur here. Some analogous reactions have been reported in the literature describing the decarbonylation of methanol by applying $RuHCl(PPh_3)_3$, where a ruthenium hydride complex $RuH_2(\eta^2\text{-}HCHO)(PPh_3)_3$ was suggested as an intermediate.[45] Furthermore, adding methanol to $WH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4$, a well-characterized η^2-formaldehyde complex $WH_2(\eta^2\text{-}HCHO)(PMe_3)_4$ was formed.[46] Therefore, notwithstanding the unknown intermediates, based on the ^{1}H NMR observation (Fig. 2a–c), it is reasonable to suppose that the alcohol decarbonylation occurred by a metal–aldehyde dihydride complex, $RuH(\eta^2\text{-}OCH_2R)(PPh_3)_2$ (**L^n**).

Furthermore, after the elimination of hydrogen from the catalyst, the intermediate reacted with H_2 produced during the reaction, to recover the catalysts. Owing to these possible interactions, the higher activity in alcohol is unsurprising. A proposed mechanism for the reaction of the ruthenium hydride with alcohol is depicted in Scheme 3.

The fact that the activity in methanol was not as high as in 2-butanol as solvent is a consequence of the difference in vapor pressure. At 80 °C methanol evaporates, excluding the mechanism described above almost completely. Moreover, performing the same experiments in open air using solvents and substrates directly from the bottle (as received), similar conversions were obtained. The high stability of the new catalysts makes the reaction conditions very convenient, enhancing the catalyst lifetime and allowing lower catalyst loadings to be applied.



Scheme 3. Proposed mechanism for decarbonylation of RCH_2OH with ruthenium hydride.

Conclusion

In conclusion, an *in situ* series of ruthenium hydride complexes $RuH(PPh_3)_2(CO)(L^n)$ (n = **a**–**h**) incorporating a Schiff base ligand was developed and investigated as isomerization catalysts. In contrast to what has been observed for ruthenium hydride catalysts described in the literature, a noteworthy advantage of these new catalysts is their inertness toward air and moisture. This advantage is related to the coordination of a Schiff base ligand. This also results in enhancement of the catalyst lifetime and thus a lower catalyst loading can be applied. Also, careful pretreatment of solvents and substrates is unnecessary, since the reaction can be performed in the open air, whereupon monitoring of the reaction progress becomes very convenient.

The complexes were tested for their isomerization performance without and with various solvents and the different behaviors of the ruthenium catalysts were explained. All the new species revealed higher activities than the parent precursor.

These observations show that modification of the Schiff base ligand can induce substantial changes in the reactivity of the corresponding catalyst. The obtained results, that all the nitro-substituted complexes performed better than the non-nitro-substituted ones and that all catalysts showed the best performance in 2-butanol, suggest that the catalytic activity strongly depends on the steric and electronic environment of the ruthenium as well as on the solvent used. Further fine-tuning of the Schiff base ligands will improve the potential of these catalytic systems in the field of isomerization.

Finally, the results of the present investigation suggest a promising application of a new family of organoruthenium (II) hydride Schiff base complexes. The fact that hydride catalysts have been reported for transfer hydrogenation and exhibit good isomerization activities (our work) would allow them to combine these two methodologies with some interesting properties by using new substrate combinations. Further studies concerning these points are currently underway.

Acknowledgments

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