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Hydroformylation-hydrogenation and hydroformylation-acetalization reactions catalyzed by ruthenium complexes

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This paper is dedicated to Prof. Georgiy B. Shul'pin.

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ABSTRACT

In this work, the catalytic activity of ruthenium II and III complexes containing chloride, pyridine, phosphine and CO ligands was investigated in the hydroformylation – hydrogenation and hydroformylation – acetalization reactions. The complexes *mer*-[$RuCl_3$(dppb)(H_2O)]**(1)**, *mer*-[$RuCl_3$(dppb)(4-Vpy)]**(2)**, *mer*-[$RuCl_3$(dppb)(4-*t*Bupy)]**(3)**, *mer*-[$RuCl_3$(dppb)(py)]**(4)**, *mer*-[$RuCl_3$(dppb)(4-Phpy)]**(5)**, *mer*-[$RuCl_3$(dppb)(4-Mepy)]**(6)**, *cis*-[$RuCl_2(CO)_2$(dppb)]**(7)**, *trans*-[$RuCl_2(CO)_2$(dppb)]**(8)**, $RuCl_3 \cdot xH_2O$**(9)**, [$RuCl_2(PPh_3)_3$]**(10)** and [$RuCl_2(PPh_3)_2$(dppb)]**(11)** were used as supplied or synthesized as previously described in the literature {Where PPh_3 = triphenylphosphine, dppb = 1,4-bis(diphenylphosphino)butane, py = pyridine, 4-Mepy = 4-methylpyridine, 4-Vpy = 4-vinylpyridine, 4-*t*Bupy = 4-*tert*-butylpyridine and 4-Phpy = 4-phenylpyridine}. These complexes were used as a pre-catalysts in a hydroformylation catalytic system to produce C—C, C=O and C—O bonds, where 1-decene resulted in a formation of respective alcohol and dimethyl acetals. Several reactions were performed in order to find the best reaction conditions presenting the best conversion (64% after 24 h). The 1-decene was also used as a substrate in two type tandem reactions labeled as: hydroformylation – hydrogenation (HH) and hydroformylation – acetalization (HA) reactions. The relationship between Ru – catalyst/substrate was 1:100, without free ligands or additives, in a controlled temperature and pressure. All the products of catalytic reactions HH and HA were analyzed by CG-FID with good yields.

1. Introduction

Transition-metal-catalyzed hydroformylation reactions constitute one of the most powerful tools for C—C bond formation in organic synthesis of aldehydes [1]. Aldehydes are valuable final products and intermediates in the synthesis of bulk chemicals such as alcohols, esters, acetals and amines. Aldehydes, acetals and alcohols are important aroma compounds used as ingredients in numerous perfumes, flavors and foods [2]. Nowadays, millions of tons of olefins are converted into aldehydes by hydroformylation reactions. Not only are aldehydes of enormous importance as constituents of flavoring mixtures, but they are also products, which can be easily derived from these compounds such as hemiacetals, acetals or carboxylic acids and their esters. Special hydroformylation protocols allow the one-step production of alcohols, which are also of crucial importance as aroma compounds [3,4]. Scheme 1 describes the general route to prepare aldehyde, alcohol and dimethylacetal by a hydroformylation – hydrogenation and hydroformylation – acetalization reactions catalyzed by ruthenium complexes.

In 1969 A.E. Shilov and co-workers showed that transition metal complexes, such as Pt (II), can catalyze H/D exchange of alkenes with solvent protons in homogeneous solution, thereby laying the foundation for the now successful field of activation of C—H bond [7–9]. The substantial isolation of the products of oxidative addition of alkanes to transition metals was first achieved by Bergman [10]. In toward of this view, very few [M(hydrido)(σ-alkyl)] complexes are know, as they tend to undergo spontaneous elimination of the alkane, which represents a step in the mechanism of the

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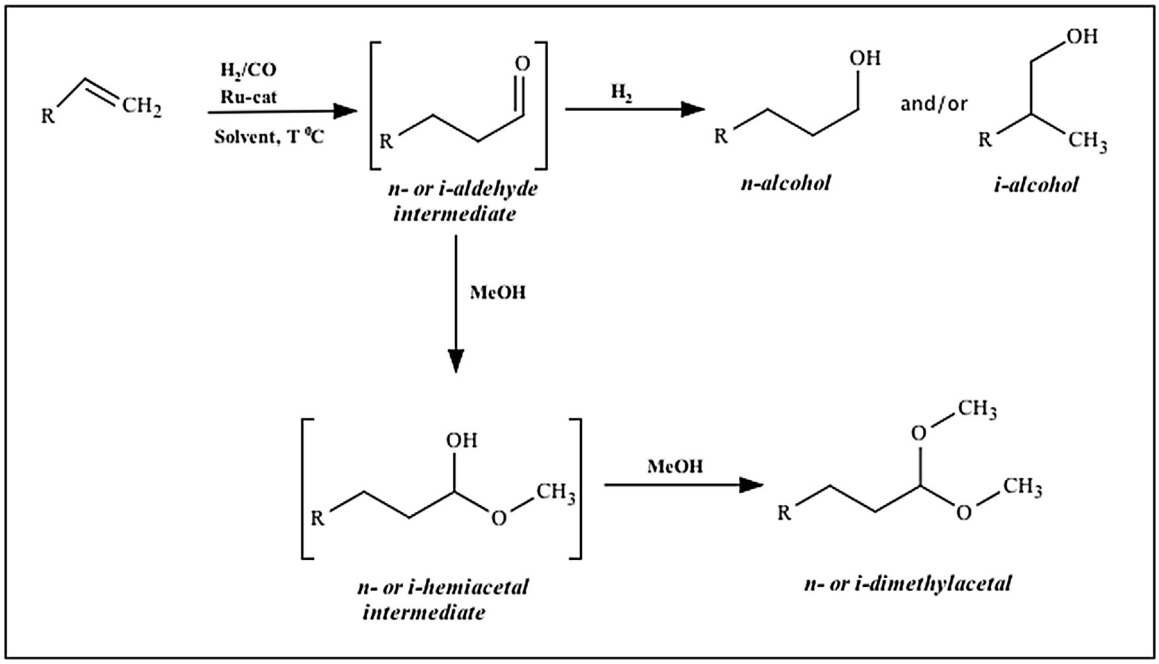


Scheme 1. Hydroformylation – hydrogenation (HH) and hydroformylation – acetalization (HA) reactions catalyzed by ruthenium complexes [5].

homogeneous catalytic hydrogenation of alkenes [6]. As a result, the activation of terminal $=CH_2$ group by transition metal complexes has the net effect of moving the C=C group along the chain of the molecule [11]. This is frequently a side reaction, desired or not according to circumstances, in other types of catalytic alkene reaction, such as hydrogenation or hydroformylation reactions. The mechanism of alkene isomerization can occurs by two different pathways, one by alkyl route, which require an M—H bond and a vacant site; and other one by allyl mechanism, which is adopted by a metal fragment that have two vacant sites but no hydrides [11] . In brief, in both mechanisms occur a C—H activation, where the transition metal complexes are capable of catalyzing the 1,3-migration of hydrogen substituent on alkene.

Ruthenium complexes have been applied to homogeneous hydroformylation reactions, as catalysts or pre-catalysts, since 1965 by Wilkinson and co-workers [12]. Since then, several ruthenium complexes containing varying ligands, such as CO, have been reported [13,14]. In the literature, hydroformylation reactions catalyzed by ruthenium complexes using different phosphines as free ligands and other additives, e.g. LiCl, are occasionally quoted [1,15]. Therefore, one of the main aims of this research was to attempt to minimize the use of free ligands and additives in order to generate minimal residues in the synthesis of alcohols and acetals, using olefins as precursors.

In a previous study, our group published the syntheses, characterization and catalytic activity of *mer*-[$RuCl_3$(dppb)(N)] (where N = derivatives pyridine ligands), in the hydrogenation of cyclohexene, undecanal and cyclohexane carbaldehyde in non-aqueous solutions [16].

Herein the catalytic activity of ruthenium II and III complexes is described, in the tandem type reactions labeled as: hydroformylation – hydrogenation (HH) and hydroformylation – acetalization (HA). Different reaction conditions were used, which include different organic substrates, solvents, temperature and pressure to produce aldehydes, alcohols and acetals.

2. Experimental section

2.1. Materials and methods

Solvents were purified by standard methods. All reagents used were of reagent grade or comparable purity, which were supplied from commercial sources: $RuCl_3 \cdot xH_2O$, triphenylphosphine (PPh_3), 1,4-bis(diphenylphosphino)butane (dppb), pyridine (py), 4-methylpyridine (4-Mepy), 4-vinylpyridine (4-Vpy), 4-*tert*-butylpyridine (4-*t*Bupy) and 4-phenylpyridine (4-Phpy) were used as received from Aldrich. All complexes used as pre-catalysts in this research were prepared as described in the literature: *mer*-[$RuCl_3$(dppb)(H_2O)]**(1)** [17], *mer*-[$RuCl_3$(dppb)(4-Vpy)]**(2)** [18], *mer*-[$RuCl_3$(dppb)(4-*t*Bupy)]**(3)** [18], *mer*-[$RuCl_3$(dppb)(py)]**(4)** [18], *mer*-[$RuCl_3$(dppb)(4-Phpy)]**(5)** [18], *mer*-[$RuCl_3$(dppb)(4-Mepy)]**(6)** [18], *cis*-[$RuCl_2(CO)_2$(dppb)]**(7)** [19], *trans*-[$RuCl_2(CO)_2$(dppb)]**(8)** [19], $RuCl_3 \cdot XH_2O$**(9)**, [$RuCl_2(PPh_3)_3$]**(10)** [20] and [$RuCl_2(PPh_3)_2$(dppb)]**(11)** [21]. For the synthesis of the hydride-ruthenium-CO complex **(7′)**, the *cis* complex **(7)** was stirred under H_2 atmosphere for 24 h in a Schlenk flask. The yellow solid was filtered off and dried in vacuum. [HRuCl$(CO)_2$(dppb)] **(7′)**: Yield: 90%. Calc. for $C_{30}H_{29}ClO_2P_2Ru$: C, 58.11; H, 4.71%. Found: C, 58.07; H, 4.78%. $^{31}P\{^1H\}$ s = 8,50 ppm and 1H $t = -10.5$ ppm and IR (KBr) ν(Ru-CO) 2065 and 2008 cm^{-1} and ν(Ru-H) 1952 cm^{-1}.

2.2. Instrumentation

Elemental analyses were performed in a Fison EA 1108 model. The FTIR spectra of the powder complexes were recorded from KBr pellets in the range of 4000 and 200 cm^{-1} range, in a Bomen-Michelson FT MB-102 instrument.

The catalytic experiments were carried out in a HEL 8 × 16 mL parallel reactor.

All NMR experiments were recorded on BRUKER DRX400 MHz equipment; in a BBO 5 mm probe at 298 K, using $CDCl_3$ (^1H) and

CH_2Cl_2 ($^{31}P\{^1H\}$) as solvents, TMS for internal reference for ^1H and the signals were labeled as s = singlet and t = triplet.

GC analysis was run on a Shimadzu CLASS-VPTM instrument using an Agilent HP-5 column (30 m, 0.32 mm diam., 0.25 μm film); carrier gas; H_2, flow rate; 0.9 mL/min. GC program for 1-decene derivatives: 50 °C (2 min) 10 °C/min until 180 °C, thereafter 30 °C/min until 320 (5 min).

2.3. Catalytic experiments

Hydroformylation experiments were carried out in a HEL 8 × 16 mL parallel reactor. The mixture substrate/Ru complex was prepared in situ. The reactor was purged with Ar (5 × 2 bar) and with syngas (5 × 5 bar). The reactor was filled with 20, 40, 90 or 100 bar syngas (CO/H_2 = 1:1) and heated to 120 or 160 °C. The pressure was kept automatically at the maximal pressure of each reaction after reaching the maximum temperature. After the reaction time ended (5 or 24 h), the reactor was cooled to room temperature. The autoclave was charged with Ru-cat (0.03 or 0.015 mmol), substrate (3 or 1.5 mmol), solvent (3 or 6 mL). The upper organic layer was analyzed by GC-FID. To promote hydroformylation – hydrogenation (HH) and hydroformylation – acetalization (HA), simple modifications were carried out in the hydroformylation protocol experiment when necessary. For details see the footnote of each table.

3. Results and discussion

3.1. Screening of reaction conditions: synthesis of alcohol

For the screening of reactions, 1-decene (**1a**) was used as a reagent yielding isomerization products *n*-decenes (**1b**), decane (**1c**), *n*- or *i*-undecanal (**1d**) and *n*- or *i*-undecanol (**1e**). The substrate/Ru-cat hydroformylation solutions were prepared in situ. In order to identify the optimal solvent, experiments were performed screening three solvents (CH_2Cl_2, toluene and *N*-methyl-2-pyrrolidone (NMP)). In an attempt to find the optimal pressure, two experiments were performed increasing the syngas pressure from 20 to 40 bar (Table 1). The hydroformylation of the C=C bond, in the reagent 1-decene, occurred to form C—C, C=O and C—O bonds in the aldehyde/alcohol products (See Table 1).

Complexes **(1)** and **(4)** were the most active complexes, which gave 32% of maximal conversion, with TOF average of 6.2 h^{-1}. It can be observed in Table 1 that the main product is the isomerized olefins in all reactions. The formation of desired products (**1d** + **1e**) was 6% (isolated yield) in the best case, using **(3)** and **(4)** as pre-catalysts with a syngas pressure of 40 bar. Table 1 shows that by increasing the syngas pressure from 20 to 40 bar, the desired product (**1d** + **1e**) also increases, but not as significantly, therefore additional catalytic experiments were conducted to improve the conversion and product yields.

3.2. Variation of substrates: synthesis of alcohol

In order to synthesize alcohols using olefins as initial material, the reactions with 1-decene **1a** and cyclohexene **2a** were performed. Due to the fact that the three solvents tested (See Table 1) did not allow sufficient conversion, it was decided to use THF and propylene carbonate (PC). Moreover, higher pressure and temperatures were applied than the experiments described in Table 1. The results, listed in Table 2, shows that the conversion of **1a** and **2a** was quantitative, but only **2a** provided the product with a high yield (92% of **2e** in THF, with rate of 92 h^{-1}).

3.3. Screening of reaction conditions: synthesis of acetals

In Table 3, the same reactions performed in Table 1 are listed, however using MeOH as a solvent in order to produce dimethylacetal instead of alcohol. It can be observed that by increasing the pressure to 40 bar, the formation of the product **1f** was also increased, 18% in the best case, with 37% of selectivity at a rate of 20 h^{-1}. For the screenings of the acetalization reaction, the same ruthenium complexes **(1)** to **(6)** were used, shown in Table 1 as pre-catalysts in the hydroformylation of 1-decene **1a**. The experiment was carried out using a pressure of 20 or 40 bar, and as expected, by increasing the pressure it was possible to diminish the formation of the isomerized olefins **1b** (*n*-decenes) and improve the formation of the desired product, dimethylacetal **1f**. However, the TOF values decreased at a high pressure, reflecting in the conversion values.

In the literature, it can be observed that it is common to add organic ligands (e.g. phosphines) and additives (e.g. LiCl) [14,22] in order to improve the yield. According to this, xantphos was added as a free phosphine and LiCl as an additive. It can be observed in Table 4 that the conversion increased considerably, but the formation of *n*-decenes (the isomerization of 1-decene) also increased and they were kept as main products, with selectivity around 50%. On the other hand, the formation of the desired product, dimethylacetal, remained low.

As it was not possible to observe any significant changes in the results using xantphos and LiCl, more attention was given to the reactions without free phosphine or additives in order to attempt to reduce the generated waste. The best results of the synthesis of undecanal dimethylacetal were obtained using high pressure (100 bar) of syngas (H_2/CO 1:1) and a high temperature of 160 °C, within 24 h, when complexes **(2)** and **(10)** were used as pre-catalysts, see Table 5. As expected, the TOF values were decreased, at a rate of 4.2 h^{-1}, but the amount of the desired product increased considerably.

3.4. Variation of ruthenium catalysts in acetalization

Eleven ruthenium II and III complexes, containing various ligands, were applied as pre-catalysts to hydroformylation-acetalization reactions of 1-decene in order to obtain the maximal conversion of the isolated product of undecanal dimethylacetal **1f**. Thus, various reactions were carried out and the results showed that **(2)** and **(10)** reported good results, and more than 60% of isolated undecanal dimethylacetal was produced. This is very promising due to the fact that acetals are products of high economic value [23].

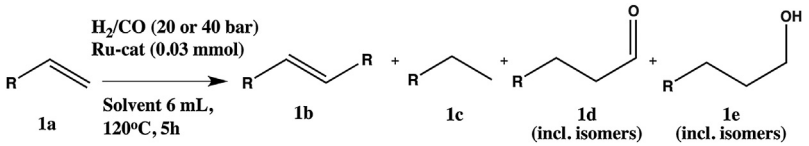
3.5. Variation of alcohols in acetalization

For the synthesis of cyclic acetals, ethylene glycol or 1,3-propanediol were used as a solvent. After 24 h under a pressure of 90 bar, the crude product was extracted with pentane/Et_2O (1:1; 3 × 5 mL). The organic phase was washed with aqueous $NaHCO_3$ (2 × 5 mL). Therefore, 1,3-propanediol afforded a higher yield of the corresponding acetal, 59% isolated yield with 84% of selectivity. In the presence of ethylene glycol, 24% of isolated yield was obtained, 53% of selectivity (See Table 6). Apparently the formation of a six – membered ring is thermodynamically favored over the formation of a five-membered ring acetal [24].

3.6. Structure and reactivity of the pre-catalysts

It is known that *mer*-[$RuCl_3$(dppb)(H_2O)], as well as *mer*-[$RuCl_3$(dppb)(N)] [N = pyridine and derivatives] are reduced, in the presence of H_2, forming the binuclear compounds, [Ru^{III}Cl(dppb)-(μCl)$_3$-Ru^{II}Cl(dppb)] and [RuCl(dppb)-(μCl)$_3$-Ru(dppb)(4-Vpy)]

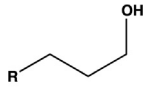
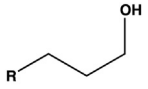
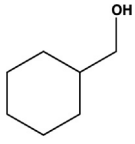
Table 1
Conversion data (%) of 1-decene **1a**, *n*-decenes **1b**, decane **1c**, undecanal – including isomers **1d** and undecanol – including isomers **1e**, using **(1)** to **(6)** complexes as pre-catalysts.



Pre-catalysts	Pressure (bar)	Solvent	Conversion%[a]	TOF h−1[c]	1b%[b] (S%)[d]	1c% (S%)[d]	1d + 1e%[b] (S%)[d]
(1)	20	CH_2Cl_2	30	6.0	24 (80)	0	0
		Toluene	24	4.8	17 (71)	0	0
		NMP	21	4.2	17 (81)	<1.0	0
(2)	20	CH_2Cl_2	4.0	0.8	3.0 (75)	0	0
		Toluene	5.0	1.0	2.0 (40)	0	0
		NMP	8.0	1.6	5.0 (63)	0	2 (25)
(3)	40	CH_2Cl_2	12	2.4	4.0 (33)	0	1
		Toluene	18	3.6	12 (67)	0	1
		NMP	16	3.2	10 (63)	<1.0	6 (37)
(4)	40	CH_2Cl_2	13	2.6	4.0 (31)	0	1
		Toluene	32	6.4	25 (78)	<1	1
		NMP	32	6.4	13 (41)	1	6 (19)
(5)	20	CH_2Cl_2	10	2.0	3.0 (30)	0	1
		Toluene	9.0	1.8	4.0 (44)	0	0
		NMP	21	4.2	19 (90)	<1.0	2 (9.0)
(6)	20	CH_2Cl_2	9.0	1.8	2.0 (22)	0	0
		Toluene	10	2.0	6.0 (60)	0	0
		NMP	6.0	1.2	5.0 (83)	0	<1

Reaction conditions: Ru-cat 0.03 mmol, 1-decene **1a** 3 mmol, H_2/CO 20 or 40 bar, solvent 6 mL, 120 °C, in 5 h.
[a] GC yield.
[b] Calculated yield by internal standard (IS = dodecane).
[c] TOF (h^{-1}) turnover frequency = $n_{pro}/(n_{cat} \times t)$. where n_{pro} = mol number of product, n_{cat} = mol number of catalyst and t = reaction time (h^{-1}).
[d] Selectivity = yield of product/conversion × 100; CH_2Cl_2–methylene chloride; NMP – N-methyl-2-pyrrolidone.

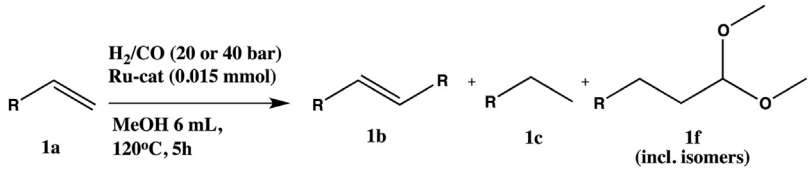
Table 2
Conversion data (%) of 1-decene **1a**, cyclohexene **2a**, undecanol – including isomers 1e and ethanol cyclohexane **2e**, using the complexes **(1)** and **(5)**, as pre-catalysts.

Pre-catalyst	Substrate	Solvent	Conversion%[a]	TOF (h^{-1})[c]	Product	Product%[b] (S%)[d]
(5)	 **1a**	THF	99	4.1	 **1e (incl. isomers)**	23 (23)
(5)	 **1a**	PC	100	4.2	 **1e (incl. isomers)**	16 (16)
(1)	 **2a**	THF	100	4.2	 **2e**	92 (92)

Reaction conditions: Ru-cat 0.015 mmol, 1-decene **1a** or cyclohexene **2a** 1.5 mmol, H_2/CO 90 bar, solvent (THF—tetrahydrofuran and PC—propylene carbonate) 6 mL, 160 °C, in 24 h.
[a] GC yield.
[b] Calculated yield by internal standard (IS = dodecane).
[c] TOF (h^{-1}) turnover frequency = $n_{pro}/(n_{cat} \times t)$; where n_{pro} = mol number of product, n_{cat} = moles number of catalyst and t = reaction time (h^{-1}).
[d] Selectivity = yield of product/conversion × 100.

[17,18,25]. Concerning this point of view, after the reaction with the pre-catalyst **(5)** described in Table 5, the solvent was evaporated and the obtained solid was dried. This isolated yellow solid labeled as **(5′)** was analyzed using IR and ^{1}H NMR techniques. The compound (**5′**) showed three strong bands in the IR spectra at 2051, 1988 and 1968 cm^{-1}, which were attributed to $\nu_{Ru\text{-}CO}$, $\nu_{Ru\text{-}CO}$ and $\nu_{Ru\text{-}H}$ bonds, respectively [26,27]. The IR spectra of the synthesized compound [$HRuCl(CO)_2(dppb)$]**(7′)** presented two bands attributed to $\nu_{(Ru\text{-}CO)}$ at 2065 and 2008 cm^{-1} and one band attributed to $\nu_{(Ru\text{-}H)}$ at 1958 cm^{-1}, see Figs. 1 and 2 in the Supplementary material (SM). The presence of hydride was also observed in the ^{1}H NMR spectrum, which was observed as a triplet at δ −10.8, which is in agreement with the heteronuclear coupling between the hydride and biphosphine ligand (dppb), (see Fig. 3 SM). The presence of a singlet at δ 11.8 in the ^{1}H NMR is attributed to the dissociation and protonation of the N-heterocyclic ligand. Therefore, these results suggested

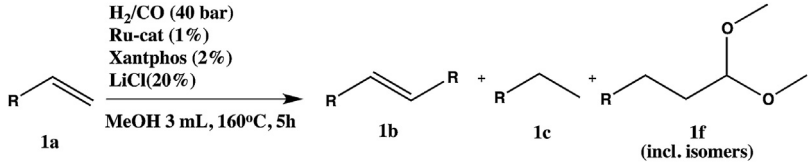
Table 3
Conversion data (%) of 1-decene **1a**, *n*-decenes **1b**, decane **1c**, undecanal dimethylacetal – including isomers **1f**, using **(1)** to **(6)** complexes, as pre-catalysts.



Pre-catalysts	Pressure (bar)	Conversion%[a]	TOF h^{-1}[c]	1b%[b] (S%)[d]	1c%	1f%[b] (S%)[d]
(1)	20	86	34	46 (53)	<1	3.0 (3.0)
(2)	20	68	27	37 (54)	<1	4.0 (6.0)
(3)	40	32	13	14 (44)	<1	12 (38)
(4)	40	49	20	18 (37)	<1	18 (37)
(5)	20	78	31	46 (59)	<1	6.0 (8.0)
(6)	20	54	22	27 (50)	<1	5.0 (9.0)

Reaction conditions: Ru-cat 0.03 mmol, 1-decene **1a** 3 mmol, H_2/CO 20 or 40 bar, MeOH 6 mL, 120 °C, in 5 h.
[a] GC yield.
[b] Calculated yield by internal standard (IS = dodecane).
[c] TOF (h^{-1}) turnover frequency = $n_{pro}/(n_{cat} \times t)$; where n_{pro} = mol number of product, n_{cat} = mol number of catalyst and t = reaction time (h^{-1}).
[d] Selectivity = yield of product/conversion × 100.

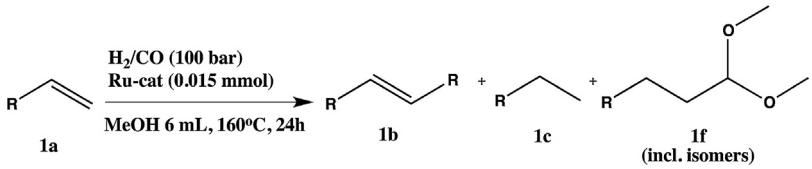
Table 4
Conversion data (%) of 1-decene **1a**, *n*-decenes **1b**, decane **1c**, undecanal dimethylacetal – including isomers **1f**, using **(1)** and **(2)** complexes as pre-catalysts.



Pre-catalyst	Additives	Conv. (%)[a]	TOF h^{-1}[c]	1b%[b]$_{(S\%)}$[d]	1[c] %	1f%[b]$_{(S\%)}$[d]
(1)	–	100	20	71(71)	0	2.0 (2.0)
	Xantphos	95	19	56 (59)	0	3.0 (3.0)
	LiCl	100	20	61 (61)	0	1.0 (1.0)
	Xantphos + LiCl	96	19	55 (57)	0	3.0 (3.0)
(2)	–	100	20	64 (64)	0	1.0 (1.0)
	LiCl	100	20	58 (58)	0	2.0 (2.0)
	Xantphos + LiCl	95	19	49 (52)	0	4.0 (4.0)

Reaction conditions: Ru-cat 0.015 mmol, 1-decene **1a** 1.5 mmol, H_2/CO 40 bar, MeOH 6 mL, 160 °C, in 5 h, Xantphos 2%, LiCl 20%.
[a] GC yield.
[b] Calculated yield by internal standard (IS = dodecane).
[c] TOF (h^{-1}) turnover frequency = $n_{pro}/(n_{cat} \times t)$; where n_{pro} = mol number of product, n_{cat} = mol number of catalyst and t = reaction time (h^{-1}).
[d] Selectivity = yield of product/conversion ×100.

Table 5
Conversion data (%) of 1-decene **1a**, *n*-decenes **1b**, decane **1c**, undecanal dimethylacetal – including isomers **1f**, using **(1)** to **(11)** complexes as pre-catalysts.



Pre-catalysts	Conversion (%)[a]	TOF h^{-1}[c]	1b (%)[b] (S%)[d]	1c (%)	1f (%)[b] (S%)[d]
1	93	3.8	30 (32)	1	31 (33)
2	100	4.2	13 (13)	<1	61 (61)
3	99	4.1	33 (33)	<1	38 (38)
4	97	4.0	39 (40)	<1	50 (52)
5	99	4.1	33 (33)	<1	51 (52)
6	93	3.8	49 (53)	0	44 (47)
7	98	4.1	30 (31)	0	38 (39)
8	91	3.8	30 (33)	<1	25 (27)
9	100	4.2	36 (36)	0	30 (30)
10	99	4.1	14 (14)	4	65 (65)
11	98	4.1	15 (15)	1	54 (54)

Reaction conditions: Ru-cat 0.015 mmol, 1-decene **1a** 1.5 mmol, H_2/CO 100 bar, MeOH 6 mL, 160 °C, in 24 h.
[a] GC yield.
[b] Calculated yield by internal standard (IS = dodecane).
[c] TOF (h^{-1}) turnover frequency = $n_{pro}/(n_{cat} \times t)$; where n_{pro} = mol number of product, n_{cat} = mol number of catalyst and t = reaction time (h^{-1}).
[d] Selectivity = yield of product/convertion × 100.

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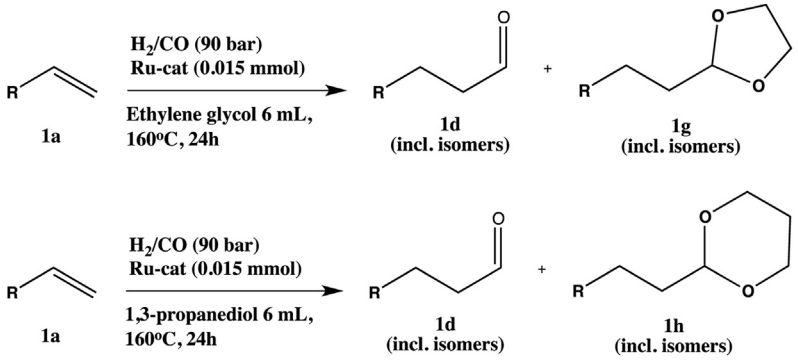
Table 6
Conversion data (%) of 1-decene **1a**, *n*-undecanal **1d**, 2-decyl-1,3-dioxalane – including isomers **1 g** and 2-decyl-1,3-dioxane – including isomers **1 h**, using complex **(5)**, as catalysts.



Pre-catalyst	Solvent	Conversion (%)[a]	TOF h^{-1}[c]	Product	Products%[b] (S%)[d]
5	Ethylene glycol	45	1.9	**1g**	24 (53)
	1,3-propanodiol	70	2.9	**1h**	59 (84)

Reaction conditions: Ru-cat 0.015 mmol, 1-decene **1a** 1.5 mmol, H_2/CO 90 bar, solvent 6 mL, 160 °C, in 24 h.
[a] GC yield.
[b] Calculated yield by internal standard (IS = dodecane).
[c] TOF(h^{-1}) turnover frequency = $n_{pro}/(n_{cat} \times t)$; where n_{pro} = mol number of product, n_{cat} = mol number of catalyst and t = reaction time (h^{-1}).
[d] Selectivity = yield of product/conversion × 1000.

that the complexes from **(1)** to **(6)**, *mer*-[$RuCl_3$(dppb)(N)] react with similarity, when they are applied to hydroformylation reactions. However, it can be observed that the behaviors of the complexes have a different performance, related to the conversion value, in mild conditions of reactions, such as low temperature and low pressure of syngas (see Tables 1 and 3). At first glance, these adverse results are attributed to displacement of the *N*-heterocyclic ligand, which is a kinetic pathway with a singular rate constant for each ligand. (see the results in Tables 2, 4 and 5). In other words, in severe conditions of temperature and pressure, the kinetic limiting pathway could be another one, where the real catalytic species could be obtained in situ without spending much time. However, it is well known that catalysts, which are generated in a fast condition, can increase the amount of side products. This behavior was observed in some reactions described above where the TOF number was around 30 h^{-1}. However, when the TOF number was controlled at lower rates, the amount of the desired products increased considerably, with selectivity over 80%.

4. Conclusion

Aldehydes, alcohols and acetals are important intermediates and products for the industrial production of bulk chemicals, perfumes and flavors. They are an important part of organic synthesis chemistry and have high economic value. Thus, several ruthenium II and III complexes were tested in hydroformylation-hydrogenation reactions to produce different alcohols and hydroformylation-acetalization reactions to produce dimethylacetals and cyclic acetals. The obtained results were good, with a production of 92% (isolated yield) of ethanol cyclohexane, 65% of undecanal dimethylacetal and 59% of 2-decyl-1,3-dioxane. For these results, the use of a free ligand or an additive was not required. These ruthenium complexes are highly versatile, as it is possible to obtain aldehydes, alcohols, dimethylacetals and cyclic acetals by simply changing the solvent and the synthesis gas.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2016.09.020.

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