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Promising Recyclable Ionic Liquid-Soluble Catalytic System for Reductive Hydroformylation

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Abstract:

We report here the reductive hydroformylation of methyl 10-undecenoate (issued from castor oil) in a biphasic liquid/liquid system. The rhodium/amine catalytic system is immobilized in an ionic liquid phase whereas the olefin and the products are in a non-polar layer. The effects of various reaction parameters (nature and concentration of amine, nature of ionic liquid, temperature and syngas pressure or composition) were studied in order to increase the production of primary alcohols. For the optimized conditions, potassium *N*,*N*-dimethyltaurinate salt associated with rhodium, immobilized in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, allowed to reach 93% of alcohols yield. Unexpectedly, with only 2 equivalents of amine with respect to rhodium, the catalytic system can be efficiently immobilized in ionic liquid and recycled due to the ionic nature of the involved catalytic species.

Introduction

The reductive hydroformylation (also known as hydrohydroxymethylation - HHM) is the direct conversion of alkenes to alcohols. This reaction consists of the catalytic transformation of carbon-carbon double bonds into primary alcohol functions via a hydroformylation reaction, followed by a hydrogenation reaction. [1,2,3,4,5] Shell company described this reaction by using a homogeneous catalytic system based on cobalt, nevertheless drastic conditions were necessary and a poor selectivity was reached.[6] The catalytic systems based on rhodium are more efficient. More precisely, rhodium catalysts associated with trialkylamines in the presence of CO/H_2 are the more interesting combinations.[7,8,9,10,11,12,13,14,15,16,17,18,19] These processes present some advantages since no oxidable phosphane is used and the two consecutive reactions can take place in the same reactor under the same reaction conditions (catalyst, temperature, pressure). In order to recover the expensive rhodium catalyst in homogeneous catalytic processes, different approaches were recently developed such as biphasic catalysis (triethanolamine or water as heavy phase) or a switchable solvent system based on CO_2.[20,21,22] Karakhanov and coll. reported a biphasic Rh catalytic system for reductive hydroformylation of 1-octene with triethanolamine as amine ligand and polar phase (ratio N/Rh=860).[20] This catalytic polar phase can be used in six sequential reactions, at least, without any significant decrease of the alcohols yields. The leaching of rhodium to non-polar phase was not really measured but evaluated by testing the non-polar phase in hydroformylation of 1-hexene. The conversion of olefin was low and no trace of alcohols was evidenced. Vorholt and coll. described a rhodium/water-soluble alkanolamine catalytic system (ratio N/Rh=400) able to transform 1-octene to alcohols in aqueous biphasic medium.[21] The influence of the amine nature on the process performances was studied as well as the rhodium leaching to the non-polar phase (between 0.5% and 16%). After optimizing the reaction parameters, recycling experiments were conducted. Even if the catalyst recycling after 5 runs was successful, the alcohol yield decreased after each run. This was attributed to an amine leaching, so a replenishment of the amine was necessary to obtain a stable catalyst recycling. The rhodium leaching varied from 1% to 12%, depending on the reaction conditions. Vorholt and coll. also described a water/alkanolamine-based CO_2-switchable solvent system for rhodium reductive hydroformylation of 1-octene to yield alcohols.[22] The alkanolamine served two functions in this system: ligand (ratio N/Rh=1000) and solvent of the catalytic system. After investigating the separation (by adding CO_2 leading to the formation of ammonium species) and the reaction parameters, catalysts recycling experiments were performed. The recycling experiments resulted in stable catalytic activity over at least three reaction runs. Afterwards, a lower aldehyde hydrogenation activity was observed (for the 7 following recycling cycles). 37% of the total rhodium was lost during these sequences.

In the field of organometallic biphasic catalysis, ionic liquids (ILs) have been proven to be useful in terms of improving catalyst performance and facilitating the catalyst-products separation.[23,24,25,26,27,28,29,30,31] It is well known that ILs can be functionalized flexibly by varying the nature of cations and/or anions with specific functionalities. Although ILs have been used for hydroaminomethylation reaction,[32] the rhodium/trialkyl amine catalytic system for reductive hydroformylation in a ionic liquid (IL) was never described.

So, we report here the reductive hydroformylation of methyl 10-undecenoate (MU) in IL. MU is easily synthesized from renewable castor oil[33] and is used for the production of Rilsan© or other interest products.[34] In addition, once functionalized, saponified and neutralized, the bifunctional compound (alcohol / carboxylic acid) is a potential starting material for the production of polymers. The effects of various reaction parameters (nature and concentration of amines, nature of ILs, temperature and syngas pressure or composition) were studied in order to increase the production of primary alcohols. The recyclability of the catalytic system and the extension to other substrates were also evaluated.

Experimental Section

All reactions involving metal-amine catalysts were performed under an air atmosphere. The catalytic precursor $Rh(acac)(CO)_2$ was purchased from Strem Chemicals and used as received. The different polar amines were purchased from Fisher Scientific or Merck, excepted for dimethyltaurinate salts which have been synthesized from commercial taurine. MU and ionic liquids were supplied by Merck. Syngas ($CO:H_2$/1:1) and dihydrogen were provided by the Linde Group in cylinders pressurized at 150 and 200 bar, respectively. The catalytic experiments were conducted under a fume hood in a room equipped with a CO detector and an explosimeter, both connected to an alarm.

^1H and ^{13}C NMR spectra were recorded at 298 K on a Bruker Avance III HD 300 (Wissembourg, France) NanoBay spectrometer equipped with a 5 mm broadband probe BBFO with Z-gradients, operating at 7.05 T field strength (300 MHz for ^1H nuclei and 75 MHz for ^{13}C nuclei). ^1H and ^{13}C chemicals shifts were determined using residual signals of the deuterated solvents. Assignment of the signals was carried out using 1D (^1H, ^{13}C) and 2D (COSY, HSQC, HMBC) NMR experiments.

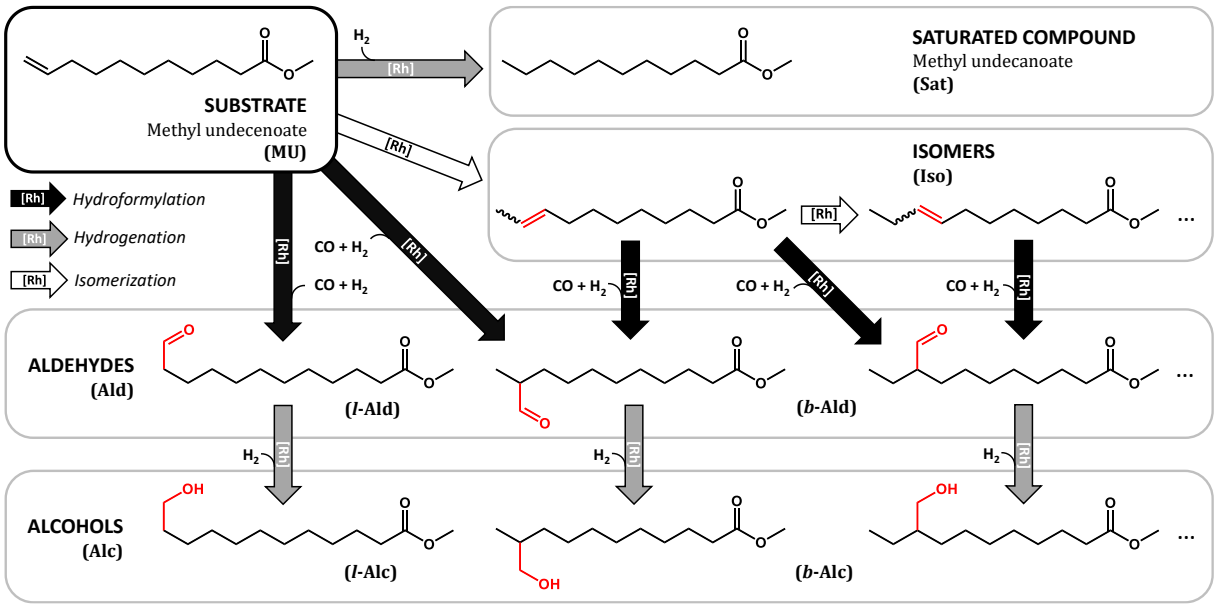
Rhodium concentrations were determined through inductively coupled plasma optical emission spectroscopy experiments using a Thermo Scientific iCAP 7000 Plus Series ICP-OES. Samples composed of an aliquot of the non-polar phase were digested before ICP experiments in a sulfuric-nitric acid/H_2O_2 mixture via microwave mineralization using a MARS 6 microwave digestion system.

In a typical catalytic experiment, $Rh(acac)(CO)_2$ (6.0 mg, 23 µmol, 1 equiv.), K-DMT (2 equiv.), methyl 10-undecenoate (1.15 g, 5.81 mmol, 250 equiv.), BMIM-NTf_2 (2.3 mL) and heptane (10 mL), were added in a 25 mL stainless-steel autoclave (Parr instrument company) equipped with a mechanical stirrer. The reactor was sealed, the reaction mixture was stirred, and the reactor was heated at 80 °C. Then, the reactor was pressurized with 80 bar of CO/H_2 (1:1). After the appropriate reaction time, the reactor was cooled to room temperature and depressurized. The lighter layer was isolated by decantation. After removing heptane by evaporation, the obtained mixture was then analyzed by NMR spectroscopy. The heavier ionic liquid layer which contains the catalytic system can then be used for a further run after addition of a fresh new mixture of methyl 10-undecenoate and heptane.

Results and Discussion

Presentation of the compounds resulting from reductive hydroformylation of MU

The reductive hydroformylation of MU by using [$Rh(acac)(CO)_2$/amine] as catalytic system and under CO/H_2 pressure can lead to different products presented in the scheme 1. MU can be hydrogenated into methyl undecanoate (Sat), isomerized into different internal olefins (Iso), hydroformylated into a linear aldehyde (*l*-Ald) or into branched aldehydes (*b*-Ald), with or without previous isomerization. Finally, the formed aldehydes can be hydrogenated into linear and branched alcohols (*l*-Alc and *b*-Alc, respectively).

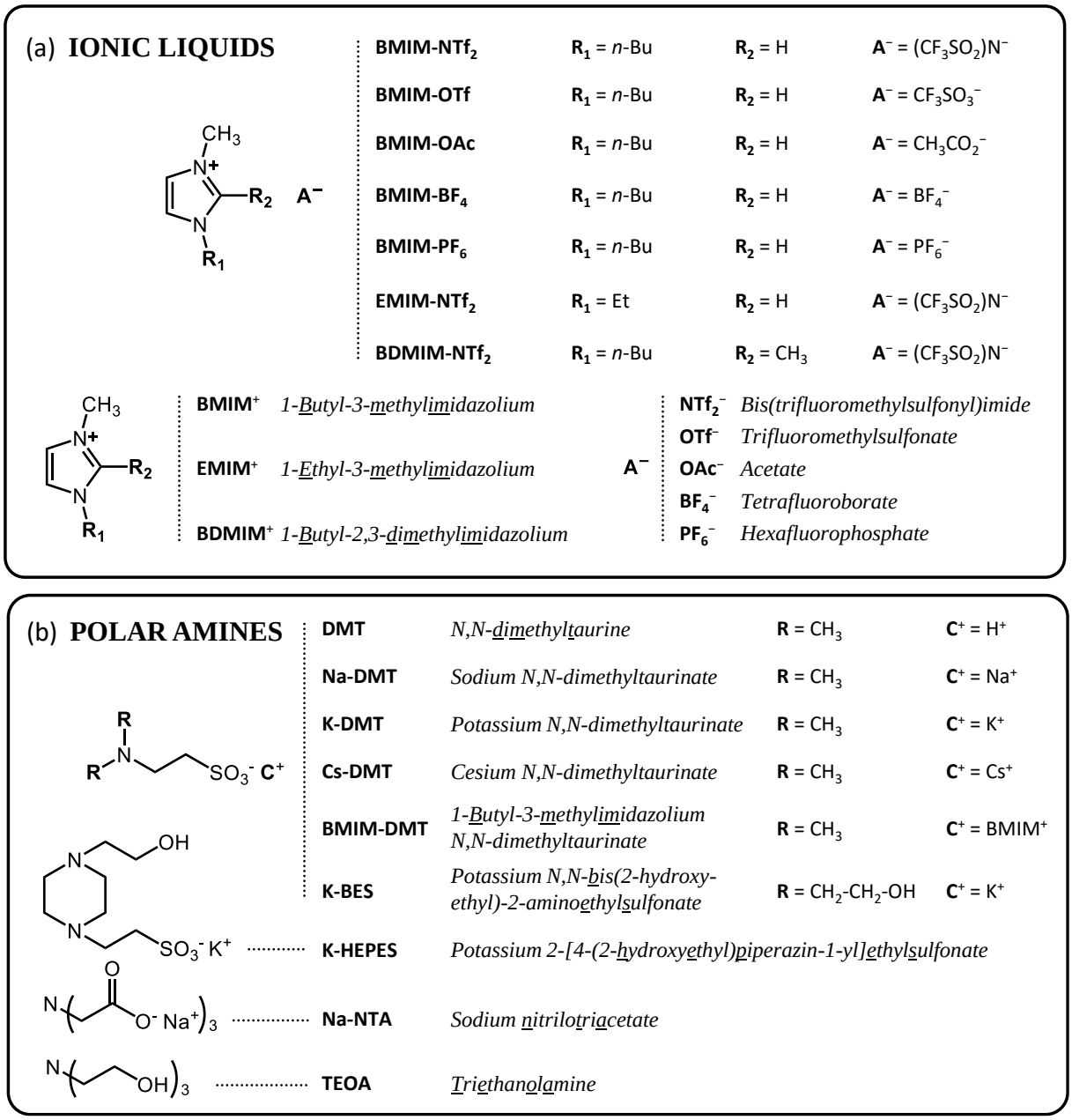


Scheme 1. Denomination of the different products coming from methyl 10-undecenoate, under reductive hydroformylation conditions.

HHM of MU: Effect of the ligand nature

For the first experiments, the classical 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-NTf_2) was chosen as IL (Scheme 2.a). This one is relatively interesting due to its combined low viscosity, broad temperature range of liquid stability, and absence of halogen atoms in potentially chemically reactive state.[35] In order to maintain rhodium species in IL, it was necessary to use ligands with affinity to IL to avoid rhodium-leaching into the non-polar layer. For this purpose, some amines were selected. More precisely, these ligands contain polar groups such as sulfonate or carboxylate or hydroxyl (Scheme 2.b). A first class of polar amines was based on *N*,*N*-dimethyltaurine (DMT), synthesized from taurine by classical Eschweiler-Clarke reaction (see SI-II.1). Particularly, different *N*,*N*-dimethyltaurinate salts were obtained as dry solids after neutralization of the sulfonic group of DMT by different bases in water, followed by a drying (see SI-II.2 for synthesis of Na-DMT, K-DMT, Cs-DMT and BMIM-DMT from DMT). K-BES and K-HEPES were obtained from reaction of BES and HEPES commercial products with KOH. Na-NTA and TEOA are commercial products. The experimental conditions used for the reductive hydroformylation involved Rh(acac)$(CO)_2$ (1 equiv.) as a rhodium precursor, a polar amine (2 equiv.) and MU (250 equiv.) under 80 bar of CO/H_2 at 80°C (Table 1). To quantify the rhodium concentration in the organic layer after reaction, inductively coupled plasma (ICP) measurements were performed.

A preliminary experiment was conducted without ligand (Table 1, entry 1). After 24 h of reaction, the analysis of the ^{1}H NMR spectrum showed that the C=C bond conversion was equal to 100 % (see SI.IV for the calculations). The yields of isomers, aldehydes and alcohols correspond to the sum of the yields of each type of products presented in the scheme 1. The different related yields were equal to 80 % for aldehydes ($Y_{(Ald)}$ (%) = 80 with a linear to branched aldehydes ratio equal to 1.0), 20 % of methyl undecanoate ($Y_{(Sat)}$ (%) = 20) and no alcohol was formed ($Y_{(Alc)}$ (%) = 0). The leaching of rhodium was very high since 33.2 % of the initial amount of rhodium was lost in the non-polar layer.



Scheme 2. (a) Ionic liquids and (b) polar amines used in this study.

For the four sulfonate ligands derivate from dimethyltaurine (Na-DMT, K-DMT, Cs-DMT and BMIM-DMT; Table 1, entries 2-5), the conversion was almost total and the yields in alcohols equal to 46%, 59%, 45% and 51%, respectively. Although the four yields were similar, the best alcohol yield was obtained with the potassium salt. The linear to branched alcohols ratios were comprised between 1.9 and 2.3 whereas the global l/b ratios were around 1.2. This last value is characteristic of a low-coordinated catalytic species, linked to both a low-coordination nature of the amine and a low steric hindrance of this latter.

At 24 h, the $l/b_{(Aldehydes)}$ ratio was always lower than the $l/b_{(Alcohols)}$ ratio, suggesting that the linear aldehyde was more rapidly hydrogenated than the branched aldehyde. Compared to the reaction performed without ligand, the leaching is largely lower in the presence of these sulfonated ligands (comprised between 2.2 and 8.4 %). These low values of leaching were unexpected and remarkable since the amount of ligand was only equal to 2 equivalents with respect to rhodium. The same experiment was performed with dimethyltaurine (DMT) (Table 1, entry 6). However, this ligand was only partially soluble in BMIM-NTf_2 and no alcohol was produced although the conversion was equal to 98%. This result was not surprising since the nitrogen doublet was not available due to the predominant zwitterion form of DMT. In addition, the Rh leaching was high since equal to 23.7%. This result undoubtedly showed that a ligand was necessary not only to maintain the rhodium species in the IL layer but also to form a catalytic species active in hydrogenation reaction. By mixing DMT and TEOA (2 equivalents of both compounds, with respect to rhodium; Table 1, entry 7), a [DMT^-, TEOA-H^+] ionic species was probably generated in situ and a nitrogen doublet was available to coordinate the rhodium. In this case, the yield in alcohols was equal to 38% with a low rhodium leaching (1.5%). For monodentate ligands bearing 2-ethylsulfonate and/or 2-hydroxyethyl groups (K-BES and TEOA), the conversions were almost total but the yields in alcohols were very low since equal to 6 and 2%, respectively (Table 1, entries 8-9). Whereas the rhodium leaching was equal to 1.9 % with K-BES, it reached 12.2 % with TEOA showing that a non-ionic ligand seems less appropriate to maintain the rhodium in IL layer. For the diamine ligand K-HEPES, the alcohols yield and the rhodium leaching were equal to 16% and 6.2%, respectively (Table 1, entry 10). The Na-NTA ligand was partially soluble in BMIM-NTf_2 and so inefficient for the production of alcohols (Table 1, entry 11). The yields in alcohols were between 45% and 59% with amines whose nitrogen atom bears one 2-ethylsulfonate group (entries 2-5), decreased with K-BES ligand whose nitrogen bears one 2-ethylsulfonate and two 2-hydroxyethyl groups (6%; Table 1, entry 8) and became almost null (2%) with three 2-hydroxyethyl groups bound to the nitrogen atom (Table 1, entry 9). These results were probably due to the electronic effect of the various groups. Indeed, some works relative of the HHM of olefins showed that the efficiency of rhodium/amine complexes to produce alcohols was directly linked to basicity of the involved nitrogen atom. [14,18,16] The stronger the electron-withdrawal effect of the groups bounded to the nitrogen, the lower the basicity of the ligand and therefore the lower the alcohols yield. Interestingly, the lowest leachings were very low since comprised between 1.5% and 2.3%.

Table 1. Methyl 10-undecenoate HHM with different polar amines [a]

Entry	Ligand	Conv.[b] (%)	$Y_{(Ald)}$[c] (%) [*l*/*b*][d]	$Y_{(Alc)}$[c] (%) [*l*/*b*][e]	*Global* [*l*/*b*][f]	$Y_{(Iso)}$[c] (%)	$Y_{(Sat)}$[c] (%)	Rh leaching (%)
1	-	100	80 [1.0]	0	[1.0]	0	20	33.2
2	Na-DMT	99	40 [0.5]	46 [2.3]	[1.1]	2	11	6.4
3	K-DMT	99	27 [0.3]	59 [2.1]	[1.2]	4	9	2.3
4	Cs-DMT	96	32 [0.5]	45 [2.2]	[1.2]	5	14	2.2
5	BMIM-DMT	99	38 [0.5]	51 [1.9]	[1.1]	6	4	8.4
6 [g]	DMT	98	86 [1.0]	0	[1.0]	0	12	23.7
7	TEOA/DMT	97	44 [0.6]	38 [2.5]	[1.1]	3	12	1.5
8	K-BES	100	73 [1.0]	6 [5.0]	[1.1]	3	18	1.9
9	TEOA	98	75 [1.1]	2 [3.0]	[1.1]	2	19	12.2
10	K-HEPES	100	65 [1.0]	16 [1.9]	[1.1]	2	17	6.2
11 [g]	Na-NTA	100	80 [1.1]	0	[1.1]	0	20	9.1

[a] Experimental conditions: $Rh(acac)(CO)_2$ (6.0 mg, 23 μmol, 1 equiv.), ligand (2 equiv.), methyl 10-undecenoate (1.15 g, 5.81 mmol, 250 equiv.), BMIM-NTf_2 (2.3 mL), heptane (10 mL), 80 bar of CO/H_2 (1:1), 80 °C, 24 h. [b] Methyl 10-undecenoate conversion. [c] $Y_{(X)}$ = yield in (X); (Ald) = aldehydes; (Alc) = alcohols; (Iso) = methyl 10-undecenoate isomers; (Sat) = saturated compound = methyl undecanoate. [d] Linear to branched ratio for aldehydes. [e] Linear to branched ratio for alcohols. [f] Global linear to branched ratio. [g] Ligand not completely soluble at this amount .

HHM of MU: Effect of the K-DMT and BMIM-DMT amount

As the best yields in alcohols were obtained with K-DMT and BMIM-DMT, the effect of the ratio Ligand/Rh was studied for these two compounds. After 24 h of reaction, by increasing the K-DMT amount from 2 to 20 equivalents with respect to Rh, similar conversions and yields were obtained (Table 2, entries 2-4 to be compare to entry 1). Only two equivalents of K-DMT are necessary which can be explained by the fact that, at higher concentration than 2 eq., this ligand was not totally soluble in BMIM-NTf_2 even after heating at 80°C during 24 h. Concerning BMIM-DMT, the switch of the counter-cation allowed to increase the solubility of the ligand in ILs.

Table 2. Effect of the K-DMT and BMIM-DMT amount on the methyl 10-undecenoate HHM [a]

Entry	Ligand (eq./Rh)	Conv.[b] (%)	$Y_{(Ald)}$[c] (%) [*l*/*b*][d]	$Y_{(Alc)}$[c] (%) [*l*/*b*][e]	*Global* [*l*/*b*][f]	$Y_{(Iso)}$[c] (%)	$Y_{(Sat)}$[c] (%)	Rh leaching (%)
1	K-DMT (2)	99	27 [0.3]	59 [2.1]	[1.2]	4	9	2.3
2 [g]	K-DMT (5)	97	19 [0.3]	60 [2.0]	[1.3]	6	12	nd [h]
3 [g]	K-DMT (10)	91	19 [0.3]	59 [2.0]	[1.3]	6	7	nd [h]
4 [g]	K-DMT (20)	99	19 [0.5]	63 [2.1]	[1.5]	10	7	nd [h]
5	BMIM-DMT (2)	99	38 [0.5]	51 [1.9]	[1.1]	6	4	8.4
6	BMIM-DMT (5)	100	27 [0.3]	61 [1.9]	[1.1]	6	6	4.3
7	BMIM-DMT (10)	100	19 [0.3]	70 [1.8]	[1.1]	5	6	4.1
8	BMIM-DMT (20)	100	34 [0.6]	24 [2.0]	[1.0]	26	16	2.4

[a] Experimental conditions: $Rh(acac)(CO)_2$ (6.0 mg, 23 μmol, 1 equiv.), ligand (K-DMT or BMIM-DMT), methyl 10-undecenoate (1.15 g, 5.81 mmol, 250 equiv.), BMIM-NTf_2 (2.3 mL), heptane (10 mL), 80 bar of CO/H_2 (1:1), 80 °C, 24 h. [b] Methyl 10-undecenoate conversion. [c] $Y_{(X)}$ = yield in (X); (Ald) = aldehydes; (Alc) = alcohols; (Iso) = methyl 10-undecenoate isomers; (Sat) = saturated compound = methyl undecanoate. [d] Linear to branched ratio for aldehydes. [e] Linear to branched ratio for alcohols. [f] Global linear to branched ratio. [g] Ligand not completely soluble at this amount. [h] Non determined.

Increasing the amount of BMIM-DMT did not affect the conversion and significantly modified the primary alcohol proportion (Table 2, entries 5-8). Indeed, the alcohol yields reached a maximum of 70% at a ratio of 10 followed by a decrease at 24% for a ratio of 20. At this ratio, the proportion of isomer and saturated products were high since equal to 26% and 16%, respectively. As already described in previous studies, [14,16] equilibria between rhodium environments could explain these catalytic results (see Figure 1). The species I and II would be able to perform hydroformylation and hydroformylation/hydrogenation reactions, respectively, whereas III and IV would be inefficient. The excess of amine amount displaced the equilibrium towards IV explaining the decrease in alcohols yield. The leaching of rhodium gradually decreased from 8.4 to 2.4 by increasing BMIM-DMT amount (Table2, entries 5-8). By comparing the both experiments performed at 2 eq. of polar amine with respect to rhodium, the values of leaching is almost four times higher in the presence of BMIM-DMT (Table 2, entries 1 and 5). BMIM-DMT is probably more soluble in the non-polar layer than K-DMT explaining the higher leaching. However, at higher ratio (5 to 20 equiv.), the rhodium is nevertheless better retained in the IL layer by this ligand.

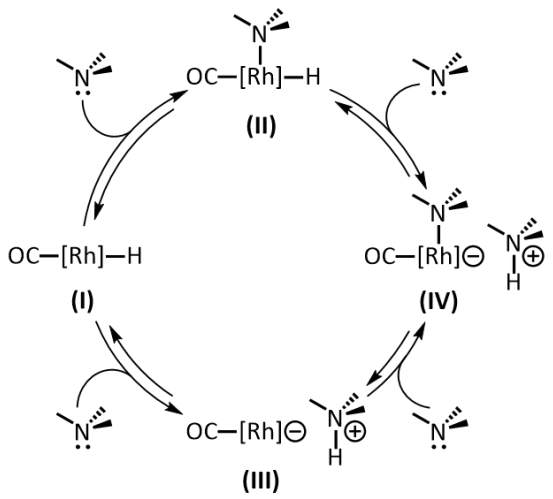


Figure 1. Different rhodium environments supposed to be in equilibrium.

To conclude this section, K-DMT, used at only 2 equivalents, appears as the best ligand to perform the reductive hydroformylation as the alcohol yields are high with a remarkably low leaching. This optimal combination will be used in the following of this study.

HHM of MU: Effect of the IL nature

Table 3. Methyl 10-undecenoate HHM with [Rh/K-DMT:1/2] catalytic system in various ionic liquids [a]

Entry	Ionic liquid	Conv.[b] (%)	$Y_{(Ald)}$[c] (%) [*l*/*b*][d]	$Y_{(Alc)}$[c] (%) [*l*/*b*][e]	*Global* [*l*/*b*][f]	$Y_{(Iso)}$[c] (%)	$Y_{(Sat)}$[c] (%)
1	BMIM-NTf_2	99	27 [0.3]	59 [2.1]	[1.2]	4	9
2	BMIM-OTf	98	62 [0.8]	21 [2.0]	[1.0]	0	15
3	BMIM-PF_6	100	67 [1.0]	20 [2.8]	[1.2]	9	4
4	BMIM-BF_4	96	78 [1.3]	6 [3.2]	[1.4]	11	2
5	BMIM-OAc	0	0	0	-	0	0
6	EMIM-NTf_2	95	41 [0.7]	40 [2.3]	[1.2]	1	13
7	BDMIM-NTf_2	99	26 [0.3]	59 [2.1]	[1.2]	3	11

[a] Experimental conditions: $Rh(acac)(CO)_2$ (6.0 mg, 23 μmol, 1 equiv.), K-DMT (2 equiv.), methyl 10-undecenoate (1.15 g, 5.81 mmol, 250 equiv.), ionic liquid (2.3 mL), heptane (10 mL), 80 bar of CO/H_2 (1:1), 80 °C, 24 h. [b] Methyl 10-undecenoate conversion. [c] $Y_{(X)}$ = yield in (X); (Ald) = aldehydes; (Alc) = alcohols; (Iso) = methyl 10-undecenoate isomers; (Sat) = saturated compound = methyl undecanoate. [d] Linear to branched ratio for aldehydes. [e] Linear to branched ratio for alcohols. [f] Global linear to branched ratio.

The effect of the counter-anion of the IL (NTf_2^-, OTf^-, OAc^-, PF_6^- or BF_4^-; see scheme 1) was firstly studied with $BMIM^+$ as counter-cation (Table 3, entries 1-5). In BMIM-OTf, BMIM-PF_6 or BMIM-BF_4, the conversion was full but the alcohols yield was lower than with BMIM-NTf_2 since equal to 21%, 20% or 6%, to be compare with 59%. With BMIM-OAc, no conversion was obtained. So, it clearly appeared that the counter-anion has an important effect on the behaviour of the reaction. These results could be explained by the fact that the NTf_2^-, OTf^-, BF_4^- or PF_6^- anions are weakly or not at all coordinated to the metal in contrast to OAc^-. In the case of acetate, the rhodium is probably highly stabilized and so inefficient as catalyst.

HHM of MU: Effect of temperature and reaction pressure

Table 4. Effect of temperature and reaction pressure on the MU HHM with [Rh/K-DMT:1/2] catalytic system [a]

Entry	T (°C)	P (bar)	CO/H_2 ratio	Conv.[b] (%)	$Y_{(Ald)}$[c] (%) [*l*/*b*][d]	$Y_{(Alc)}$[c] (%) [*l*/*b*][e]	*Global* [*l*/*b*][f]	$Y_{(Iso)}$[c] (%)	$Y_{(Sat)}$[c] (%)
1	60	80	1:1	71	46 [1.3]	10 [3.0]	[1.5]	9	6
2	80	80	1:1	99	27 [0.3]	59 [2.1]	[1.2]	4	9
3	100	80	1:1	100	24 [0.1]	65 [1.8]	[1.0]	0	11
4	120	80	1:1	100	48 [0.3]	37 [2.1]	[0.7]	0	15
5	80	60	1:1	97	44 [0.5]	33 [2.7]	[1.2]	8	12
6	80	80	1:1	99	27 [0.3]	59 [2.1]	[1.2]	4	9
7	80	100	1:1	92	21 [0.5]	62 [1.7]	[1.2]	0	9
8	80	120	1:1	100	21 [0.5]	68 [1.6]	[1.2]	0	11
9	80	80	1:2	100	28 [0.4]	50 [2.3]	[1.2]	7	14
10	80	80	1:3	100	39 [0.7]	37 [2.7]	[1.3]	10	14
11	100	100	1:1	99	20 [0.3]	72 [1.5]	[1.1]	1	6
12[g]	100	100	1:1	100	6 [0.1]	86 [1.1]	[1.0]	0	8
13	100	120	1:1	100	14 [0.1]	83 [1.3]	[1.0]	0	3
14[g]	100	120	1:1	100	3 [-]	93 [1.1]	[1.1]	0	4

[a] Experimental conditions: $Rh(acac)(CO)_2$ (6.0 mg, 23 μmol, 1 equiv.), K-DMT (2 equiv.), methyl 10-undecenoate (1.15 g, 5.81 mmol, 250 equiv.), BMIM-NTf_2 (2.3 mL), heptane (10 mL), syngas CO/H_2 (1:1), 24 h. [b] Methyl 10-undecenoate conversion. [c] $Y_{(X)}$ = yield in (X); (Ald) = aldehydes; (Alc) = alcohols; (Iso) = methyl 10-undecenoate isomers; (Sat) = saturated compound = methyl undecanoate. [d] Linear to branched ratio for aldehydes. [e] Linear to branched ratio for alcohols. [f] Global linear to branched ratio. [g] t=48 h.

With the counter-anion NTf_2^-, the influence of the cation was also studied (Table 3, entries 1, 6 and 7). In EMIM-NTf_2 and BDMIM-NTf_2, the conversions were high and the yields in alcohols equal to 40% and 59%, respectively. So, the 3 imidazolium tested cations gave similar results. Moreover, as BMIM-NTf_2 and BDMIM-NTf_2 give the same results (Table 3, entries 1 and 7), the good results obtained with BMIM-NTf_2 ionic liquid cannot be attributed to the in-situ formation of carbene ligand by deprotonation of $BMIM^+$ imidazolium cation by K-DMT ligand. Indeed, no carbene can be formed from the BDMIM imidazolium cation because of the methyl present in position 2.

The effect of the reaction temperature on the methyl 10-undecenoate HHM was studied for the catalytic system Rh/K-DMT from 60 to 120 °C, and for a pressure of CO/H_2 (1:1) of 80 bar (Table 4, entries 1-4). The conversion increased with the temperature. At 60 °C, the conversion was equal to 71% whereas 100% of conversion was reached at temperature higher than 80 °C. The yield of alcohols increased from 60 °C to 100 °C and then decreased ($Y_{(Alc)}$ = 10% at 60 °C, 59% at 80 °C, 65% at 100 °C and 37% at 120 °C). This decrease in aldehyde hydrogenation in HHM when increasing the temperature was already observed by Vorholt and coll.[21] It seems that the catalytic species active for hydrogenation are no longer stable at high temperature. The global l/b ratio decreased also with temperature (from 1.5 at 60 °C to 0.7 at 120 °C). These two tendencies can be explained by a decoordination of the amine from the rhodium atom at high temperature. At the same time, the proportions of saturated product increased, from 6% at 60°C to 15% at 120 °C, suggesting that the catalytic species responsible of alkenes hydrogenation would not be the same than that involved in aldehydes hydrogenation. The effect of the reaction pressure was also studied. When the total CO/H_2 pressure increased from 60 bar to 120 bar (Table 4, entries 5-8), the conversion was always close to 100% and the yields of alcohols increased from 33 to 68%. The yields in saturated products were stable whereas isomeric products disappeared at pressures higher than 100 bar, showing that the internal C=C were transformed into branched aldehydes then alcohols. The global l/b ratio stayed constant at a value of 1.2, whatever the total pressure, showing that the catalytic species nature was not affected in the tested pressure range. The HHM reaction consuming CO and H_2 with a ratio of 1:2, the influence of the relative proportions of CO/H_2 was evaluated by keeping a total pressure of 80 bar. The methyl 10-undecenoate conversions were total whatever the CO/H_2 ratio but the alcohols yield decreased regularly with the H_2 amount increase in the reactor ($Y_{(Alc)}$ = 59%, 50% and 37% for CO/H_2 = 1:1, 1:2 and 1:3 respectively; Table 4, compare entries 2, 9 and 10). This result showed that a sufficient amount of CO is probably required to form catalytic species active in aldehydes hydrogenation reaction, and that the ratio 1:1 is the best value. In order to try to improve the alcohols yields, two supplementary experiments were performed at 100 °C/100 bar and 100 °C/120 bar, during 24 h and 48 h (Table 4, entries 11-14). Both increases of

pressure and temperature allowed actually to produce higher amounts of alcohols. The best alcohols yield of 93% was obtained at 100 °C and 120 bar, after 48 h of reaction.

HHM of MU: Kinetic follow-up

In order to better understand the course of the HHM reaction, a kinetic follow-up of the methyl 10-undecenoate HHM at 80 °C and 80 bar was performed in the presence of the best catalytic combination Rh/K-DMT. The figure 2a shows that the formation of aldehydes starts without induction time and that alcohols are already formed after 2 hours. The aldehydes and alcohols curves of figure 2a indicate in a logical way that the alkene hydroformylation reaction and the aldehydes hydrogenation reaction are consecutive. While the amount of saturated product stabilizes at a value of 7% when terminal C=C bonds have disappeared from the medium, the amount of isomers decreases with time, giving branched aldehydes then branched alcohols, and until complete consumption at 48 h. After 48h of reaction, the yield of alcohols was equal to 85%. The figure 2b shows the evolution of the linear and branched products with time (aldehydes and alcohols). As suggesting above, it clearly appeared that the linear aldehyde was hydrogenated faster than the branched aldehyde.

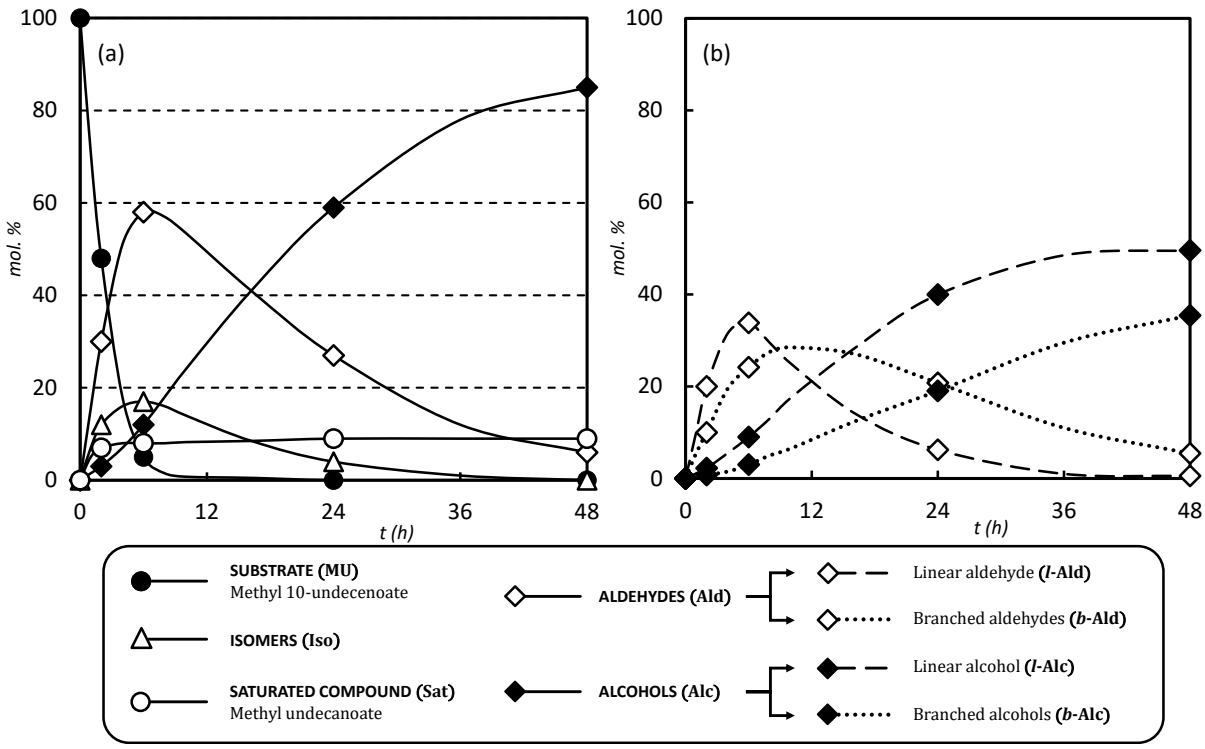


Figure 2. Kinetic follow-up of the methyl 10-undecenoate hydrohydroxymethylation. (a) Substrate transformation into the 4 kinds of products. (b) Evolution of linear and branched aldehydes and alcohols with time. Experimental conditions: $Rh(acac)(CO)_2$ (6.0 mg, 23 μmol, 1 equiv.), K-DMT (2 equiv.), methyl 10-undecenoate (1.15 g, 5.81 mmol, 250 equiv.), BMIM-NTf_2 (2.3 mL), heptane (10 mL), 80 bar of CO/H_2 (1:1), 80 °C.

HHM of other substrates

Table 5. HHM of various substrates catalyzed by the [Rh/K-DMT:1/2] system [a]

Run	Substrate	Conv.[b] (%)	$Y_{(Ald)}$[c] (%) [*l*/*b*][d]	$Y_{(Alc)}$[c] (%) [*l*/*b*][e]	*Global* [*l*/*b*][f]	$Y_{(Iso)}$[c] (%)	$Y_{(Sat)}$[c] (%)
1	Isosorbide diallyl ether	100	36 [1.2]	49 [0.9]	[1.0]	10	5
2	1-Octene	100	51 [0.8]	35 [1.8]	[1.2]	0	14
3	1-Hexadecene	100	75 [1.1]	8 [2.4]	[1.2]	2	15
4	Methyl oleate	57	37 [0]	0 [-]	[0]	nd	20
5	Ethyl ricinoleate	82 [g]	26 [0]	0 [-]	[0]	nd	3

[a] Experimental conditions: $Rh(acac)(CO)_2$ (6.0 mg, 23 μmol, 1 equiv.), K-DMT (2 equiv.), substrate (5.81 mmol of C=C, 250 equiv.), BMIM-NTf_2 (2.3 mL), heptane (10 mL), 80 bar of CO/H_2 (1:1), 80 °C, 24 h. [b] Substrate conversion excepted for entries 4 and 5: C=C double bonds conversion. [c] $Y_{(X)}$ = yield in (X); (Ald) = aldehydes; (Alc) = alcohols; (Iso) = isomers; (Sat) = saturated compound. [d] Linear to branched ratio for aldehydes. [e] Linear to branched ratio for alcohols. [f] Global linear to branched ratio. [g] Cyclic hemiacetals (36%) and ketone (17%) were also produced.

To widen the scope of this study, isosorbide diallyl ether as polar substrate and olefins (1-octene and 1-hexadecene) or commercial vegetable oils derivatives (methyl oleate and ethyl ricinolate) as apolar substrates were subjected to Rh-catalyzed HHM (Table 5). The products were analyzed by ^{1}H NMR by using similar procedures to that published previously. [16,17] The conversion was total with isosorbide diallyl ether and an alcohols yield of 49% was reached. However, at the end of the reaction, NMR analysis showed that the products were present in the IL phase and not in the heptane phase, preventing from recycling experiments. With apolar substrates, the conversions were full with 1-octene and 1-hexadecene but were not total with the vegetable oils derivatives (Table 5, entries 2 to 5). In addition, no alcohols were produced from methyl oleate and ethyl ricinoleate. It clearly appeared that the catalytic activity is dependant not only to the solubility of substrates in ILs (the more apolar the substrate, the lower the alcohol yield) but also to the position of the C=C bond (less reactivity of internal C=C). So, this described system do not efficiently work with very apolar substrates whereas it worked with less apolar substrates. The nature of the IL will have to be refined according to the nature of the substrate to be functionalized.

HHM of MU: recycling experiments

After optimizing the reaction parameters, catalyst recycling experiments were firstly envisaged with the catalytic system Rh/K-DMT (ratio of K-DMT/Rh of 2) in BMIM-NTf_2 at 80 °C, under 80 bar of CO/H_2 and with cycles of 24 h (Figure 3a). The temperature, pressure and reaction time were chosen in order

that the conversion of the aldehydes into alcohols was not complete. After, the first run (Figure 3a, run 1), the biphasic reaction mixture can be separated by simple decantation after cooling at room temperature the autoclave. The heptane upper phase containing the products of the reaction was used to determine the conversion, the yields and also to measure the rhodium leaching. The lower IL phase containing the catalyst was used for a first recycling experiment by adding a fresh organic layer containing MU and heptane in the same quantities as for run 1 (Figure 3a, run 2). Two additional runs were then successively performed giving, as the two previous runs, complete or almost complete conversions (Figure 3a, runs 3-4). However, the alcohols yield decreased from 59% to 12% whereas the yields in isomers and saturated products stayed relatively stable. For the 4 runs, the global l/b ratio was equal to 1.2 (see SI.VI.table S3 for the l/b ratios value). At the same time and although the ratio between rhodium and amine is only equal to 2, the leaching was very low since comprised between 0.5% and 1.3%. Interestingly, after the fourth run, 2 equivalents of K-DMT were added in the IL layer and the alcohols yield increased to 24% (Figure 3a, run 5). By adding a new charge of K-DMT, the production of alcohols can obviously be reactivated. The decrease observed for the three first runs could be attributed to an amine leaching to the non-polar layer. So, a reloading of K-DMT would be necessary to recover an efficient catalyst recycling. In a second time, catalyst recycling experiments were performed with the catalytic systems [Rh/BMIM-DMT:1/5] and [Rh/BMIM-DMT:1/10] in the same experimental conditions selected for [Rh/K-DMT:1/2] system (see Figure 3b and 3c, and also SI. VI, Tables S4 and S5 for the l/b ratios value). Note that BMIM-DMT was not used at 2 equivalents with respect to rhodium because the leaching was higher (8.4% - Table 2, entry 5). At 5 equivalents of BMIM-DMT with respect to rhodium, four runs were realized and a slight decrease of conversion was observed whereas the alcohols yield decreased more significantly from the first run (Figure 3b, runs 1-4). At 10 equivalents, five runs were successively performed giving complete conversions (Figure 3c, runs 1-5). The alcohols yield only decreased from the fourth run to reach 44% at the fifth run. For both ratios, the yields in isomers and saturated products stayed stable. For all the runs, the leaching was low and stable at values around 4%.

For both ligands, it is important to underline that only 2 equivalents of K-DMT or 5 or 10 equivalents of BMIM-DMT with respect to rhodium seems enough not only to perform the reaction but also to maintain a high amount of rhodium in the IL layer. Indeed, generally largely higher amount of amine with respect to rhodium (at least 400 equivalents) was necessary in homogeneous or biphasic conditions (water or triethanolamine as heavy phase). The specificity of the ionic liquid medium to effectively immobilize rhodium, even in the presence of a small amount of amine, could be due to the anionic cluster nature of the rhodium complexes involved in HHM. Indeed, it is reasonable to think that these anionic species would strongly associate with imidazolium cations.

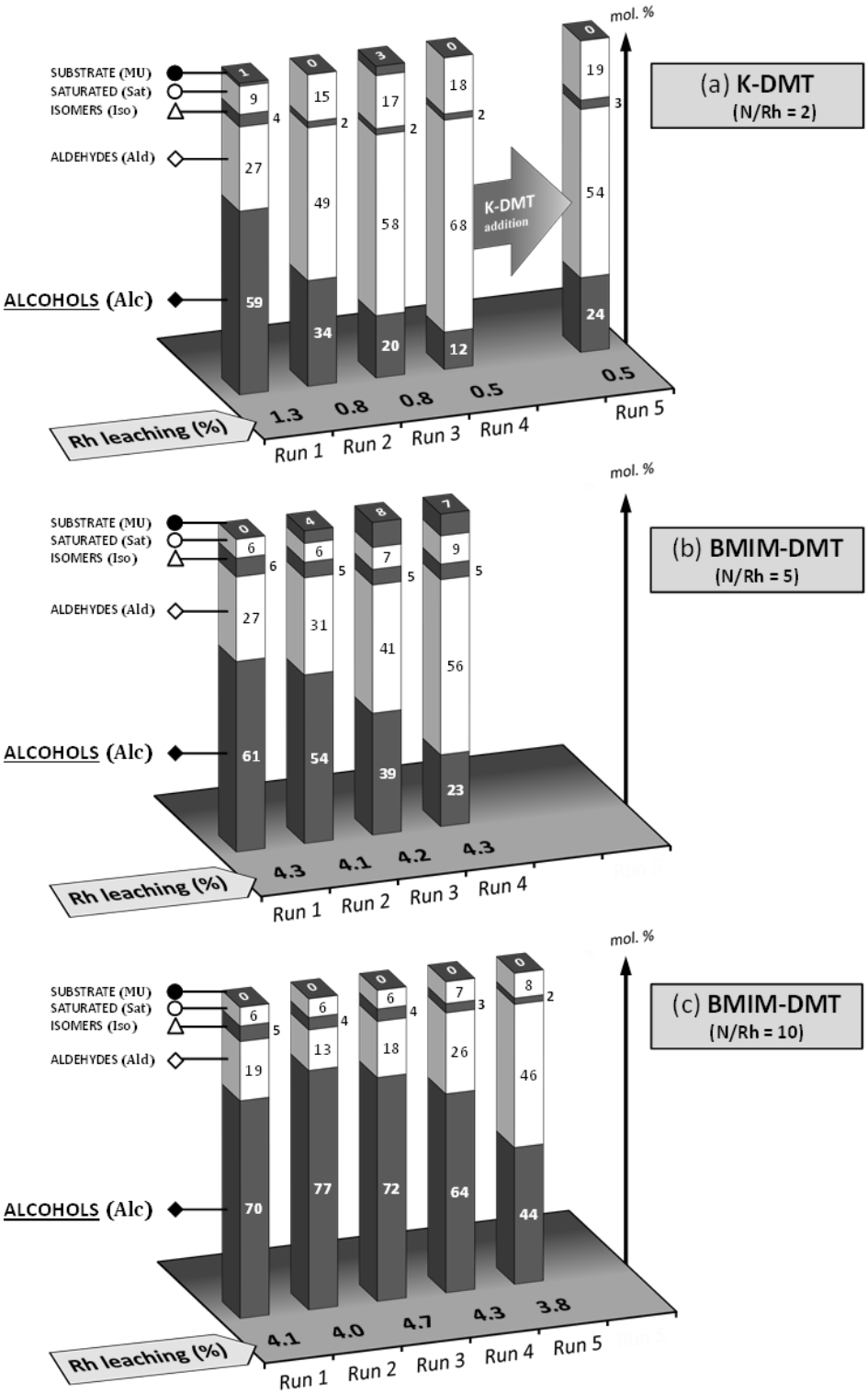


Figure 3. Rhodium leaching and relative molar amount of methyl undecenoate and products during recycling experiments of (a) [Rh/K-DMT: 1/2] system, (b) [Rh/BMIM-DMT: 1/5] system, and (c) [Rh/BMIM-DMT: 1/10]. For run 1: $Rh(acac)(CO)_2$ (6.0 mg, 23 μmol, 1 equiv.), taurinate derivative (2, 5 or 10 equiv.), methyl undecenoate (1.15 g, 5.81 mmol, 250 equiv.), BMIM-NTf_2 (2.3 mL), heptane (10 mL), 80 bar of CO/H_2 (1:1), 80 °C, 24 h. The rhodium leaching corresponds to the percentage of the initial amount of rhodium atom introduced at run 1 found in the heptane and products upper layer, after reaction. For (a), two new equivalents of K-DMT (with respect to initial amount of rhodium introduced at run 1) were added in the ionic liquid between run 4 and run 5.

Conclusion

Here we reported a biphasic rhodium catalytic system based on ILs for reductive hydroformylation reaction. Interestingly, the various amines used as ligands are efficient, from only 2 equivalents with respect to rhodium, not only to perform the reaction but also to maintain a high amount of rhodium in the IL layer. For the best combination, the catalytic IL phase can be recycled at least three times without important decrease of alcohols yield and also without an important loss of rhodium in the non-polar layer demonstrating potentiality of ILs to elaborate efficient recyclable systems.

Supporting Information

This part contains the synthesis and characterization of taurine derivatives, the synthesis and characterization of the methyl 10-undecenoate HHM products, the determination of conversion, yields, and l/b ratios for the catalytic experiments, the kinetic follow-up of the methyl 10-undecenoate HHM and the catalytic systems recycling experiments.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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