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Rhodium-Catalyzed Reductive Hydroformylation of Polyunsaturated Vegetable Oils Assisted by Triethylamine/*N*-methylimidazole Ligands Combination

Walid Abdallah,[a] Michel Ferreira,[a] Chryslain Becquet,[a] Jérémy Ternel,[a] Hervé Bricout,[a] Eric Monflier,*[a] and Sébastien Tilloy[a]

In this work, the reductive hydroformylation of linseed and sesame oils was carried out successfully by using a rhodium catalyst precursor associated to triethylamine/*N*-methylimidazole ligands combination. Interestingly, in the presence of triethylamine and *N*-methylimidazole at a precise ratio with respect to rhodium, the isomerization reaction can be inhibited and control experiments realized on methyl linoleate and methyl linolenate have clearly shown that no conjugated products were formed. This new catalytic system is full of interest since the yields in alcohols, after 24 h, are equal to 21% and 15% for Rh/triethylamine combination, whereas equal to 58% and 63% for Rh/triethylamine/*N*-methylimidazole combination, for linseed and sesame oils, respectively.

1. Introduction

Hydrohydroxymethylation (HHM), also referred to as reductive hydroformylation, is the catalytic conversion of carbon–carbon double bond into primary alcohol function under CO/H_2 pressure. This reaction is a tandem hydroformylation/hydrogenation sequence, in fact, the formed aldehyde is then reduced into alcohol. Börner et al. published in 2015, a detailed review on the production of alcohols via hydroformylation.[1] These authors differentiate the five following approaches for the production of alcohols: (i) two-step process/separate vessels/different reaction conditions; (ii) one-pot reaction/two catalysts/different reaction conditions; (iii) one-pot reaction/a single catalyst/different reaction conditions; (iv) one-pot reaction/two catalysts and (v) one-pot reaction/a single catalyst. This last approach, called auto-tandem catalysis, is the preferred way since a single catalyst, under the same reaction conditions, can perform the hydroformylation of C=C followed by the reduction of formyl into alcohol. This reaction was firstly performed by cobalt catalysts but using drastic operating conditions (high temperature and pressure).[2–4] Associated to trialkylphosphines, rhodium precursors are able to produce alcohols with more efficiency.[5–7] To avoid the use of air sensitive phosphine, nitrogen ligand can also be used.[8] Among these kinds of ligands, trialkylamines are very interesting since they are bulky available, cheap, non-oxidizable (contrary to phosphine), and easily removable at the end of the reaction. For instance, HHM can be performed with the Rh/amine catalyst system in various solvents.[9–28] Additionally, there have been reports of recycling experiments utilizing biphasic two-phase systems (such as triethanolamine, ionic liquid, or water as the heavy phase) or switchable solvent systems based on CO_2.[29–32]

The diversity of functionalized olefins by HHM is very large but only a few examples of vegetable oils were reported. More precisely, in the presence of Rh/trialkylamine as catalytic system, polyols were obtained from olive, sunflower, castor, or jojoba oils. Unfortunately, Rh/trialkylamine-catalyzed HHM of sesame or linseed oil produced only very little amounts of alcohols.[21,33] The authors explained that the polyunsaturated linoleic and linolenic chains of these oils did not yield polyhydroxytriglycerides. Indeed, isomerization of the double bonds of these polyunsaturated chains into conjugated double bonds was observed. As previously reported during rhodium/phosphine catalyzed hydroformylation reaction, conjugated systems strongly inhibit the catalytic system by the formation of a stable π-allylic rhodium complex (Scheme 1).[34–36] So, the challenge is to successfully synthesize polyols from linoleic and linolenic chains. The crucial step is to avoid the isomerization leading to conjugated double bonds.

Some of us have described that the use of *N*-methylimidazole (MIM, see Scheme 2a) as ligand did not enable the rhodium catalyzed HHM of ethyl ricinoleate (obtained by ethanolysis of castor oil) but only hydroformylation and drastically limit the isomerization reaction.[24,33] In the course of the reaction, the double C=C bond can migrate along the carbon chain to the alcohol in position 12, forming an enol that quickly tautomerizes into a ketone. With the rhodium/MIM catalytic system, the yield

[a] *W. Abdallah, Dr. M. Ferreira, Dr. C. Becquet, Dr. J. Ternel, Dr. H. Bricout, Prof. E. Monflier, Prof. S. Tilloy*
Univ. Artois, CNRS, Centrale Lille, Univ. Lille, UMR 8181, Unité de Catalyse et Chimie du Solide (UCCS), rue Jean Souvraz, SP 18, Lens 62300, France
E-mail: eric.monflier@univ-artois.fr

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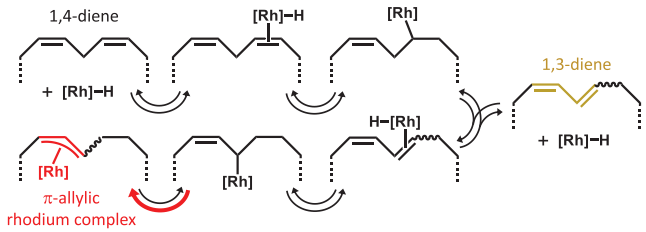
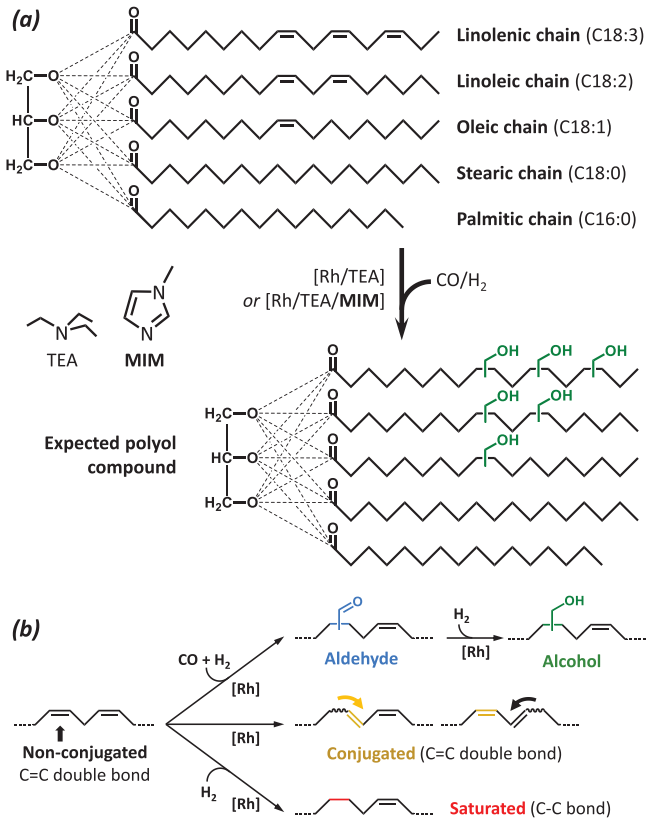


Scheme 1. Mechanism of the formation of stable π-allylic rhodium complexes by isomerization of the 1,4-diene units of polyunsaturated linoleic and linolenic chains into 1,3-diene units.



Scheme 2. (a) Schematic representation of linseed oil and its HHM reaction and (b) different possible transformations of a linseed oil C=C double bond.

in ketone was very low (inferior to 3%) whereas equal to 14%–23% with rhodium/trialkylamine catalytic system. Unfortunately, no alcohol was formed with the catalytic system rhodium/MIM, whereas alcohol was produced in the presence of rhodium/trialkylamine catalytic system. The low isomerization in the presence of MIM ligand led us to investigate in depth the effect of this compound on the rhodium/trialkylamine catalytic system conventionally used to perform the HHM reaction. The basic idea was to use a trialkylamine/MIM mixture allowing on the one hand, high alcohol yield and on the other hand, low yield for conjugated dienes. The feasibility of this approach was investigated by using a combination of rhodium, triethylamine (TEA), and MIM as catalytic system and linseed oil as model substrate. The effects of TEA/MIM ratio were particularly investigated by determining the percentages of each reaction product. The HHM of other polyunsaturated substrates such as sesame oil and the methyl esters of linoleic and linolenic acids was also reported with the optimized TEA/MIM ratio.

2. Results and Discussion

2.1. Presentation of the Compounds Resulting from Reductive Hydroformylation of Linseed Oil

The reductive hydroformylation of linseed oil using [Rh(acac)$(CO)_2$/TEA] as catalytic system and under CO/H_2 pressure can lead to different products as shown in Scheme 2. A non-conjugated C=C double bond of linseed oil can be hydrogenated to a C–C single bond ("Saturated", in scheme 2b), isomerized to a conjugated double bond ("Conjugated") itself hydrogenatable or hydroformylatable to an aldehyde function ("Aldehyde"). Finally, the formed aldehydes functions can be hydrogenated to alcohol functions ("Alcohol").

2.2. HHM of Linseed Oil by Rh/TEA Catalytic System: Optimization of Reaction Parameters and Kinetic Follow-up

The effects of various reaction parameters such as TEA amounts, solvents, temperature, pressure, and composition of syngas were first studied to find the best combinations to determine the limits of this system. All these results are compiled in supporting information in order to find the best compromise concerning the experimental conditions. So, the majority of catalytic tests were carried out by using Rh(acac)$(CO)_2$ as a rhodium precursor, triethylamine (TEA) as a ligand, and toluene as a solvent under 80 bar of CO/H_2 (1/1) at 80 °C. A kinetic follow-up reaction was performed. Figure 1 shows that conjugated double bonds are quickly formed. However, after reaching a maximum at 8 h of reaction time, the yield of conjugated double bonds decreases over time. From this point on, the yields of alcohols and hydrogenated C=C double bonds increase, while the yield of aldehydes remains below 10% (Figure 1a). This last percentage indicates that the reactions of C=C double bond hydroformylation and formyl group hydrogenation are consecutive. After 72 h, the conversion is equal to 100% and the yields of alcohols and hydrogenated products are equal to 52.5% and 47.5%, respectively.

2.3. HHM of Linseed Oil by Rh/TEA/MIM Catalytic System: Effects of the TEA/MIM Ratio

The effect of different ratios of the combination of TEA and MIM on the catalytic activity was studied to determine the yield of each reaction product with the aim of limiting the isomerization reaction. The reaction time was chosen to be 24 h, expecting the widest range of products to be quantified. Thus, a series of reactions were conducted by varying the TEA/Rh and MIM/Rh molar ratio from 0 to 2800 and 0 to 1000, respectively. All the results

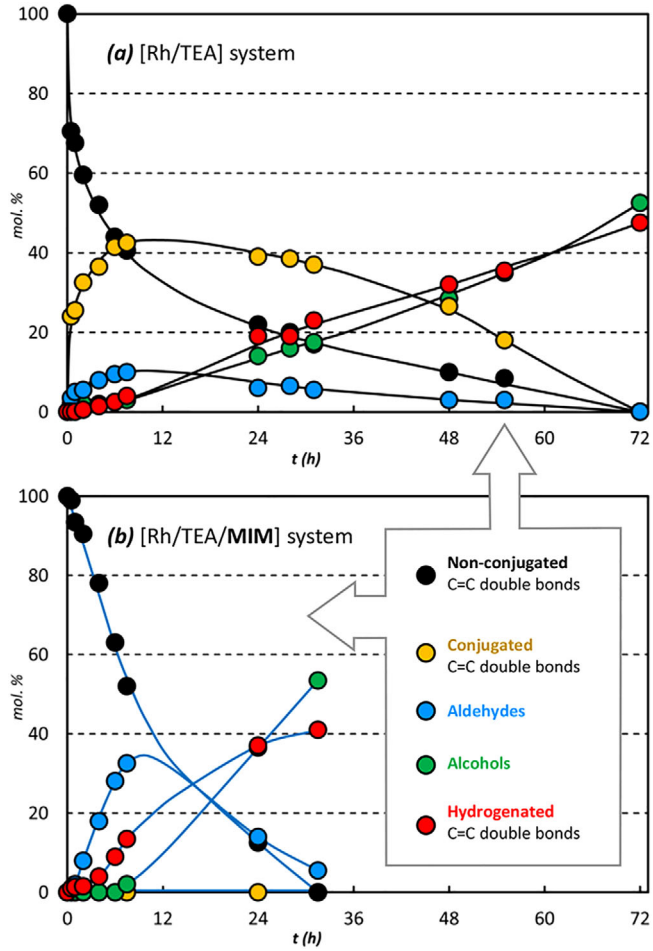


Figure 1. Kinetic follow-up of linseed oil HHM catalyzed by: (a) Rh/TEA and (b) Rh/TEA/MIM catalytic system. Experimental conditions: $Rh(acac)(CO)_2$ (42 mg, 162.7 µmol, 1 equiv), Linseed oil (6034 mg, 40.7 mmol, 250 equiv of C=C bonds), TEA (16.47 g, 162.7 mmol, 1000 equiv), MIM (without or with 2.92 g, 35.6 mmol, 220 equiv.), Toluene (amount to reach a total volume of 71.2 mL in the autoclave), 80 bar of CO/H_2 (1:1), 80 °C.

were presented in 2D graph with TEA concentration as *x*-axis and MIM concentration as *y*-axis (Figure 2). Conversion and yields are represented by spheres with diameters proportional to the values. The values of C=C double bonds conversion are comprised between 26% and 100%, nevertheless, only a high quantity of MIM has a deleterious effect on conversion. Indeed, up to 500 equivalents of MIM, conversions are between 72% and 100%. For the aldehyde yields, the highest value was reached without TEA and at 250 equivalents of MIM but in this case no alcohol was produced. In fact, the amounts of aldehyde and alcohol are linked since these products are consecutively formed. The best yield in alcohols was equal 58% for ratio TEA/MIM 1000/220 whereas equal to a maximum of 21% without MIM. The best zone was comprised for TEA/Rh ratio 1000–2000 and MIM/Rh ratio 150–250. The yields of conjugated products varied between 36% and 43% in the presence of TEA alone and in all cases, in the presence of MIM, the maximum value is equal 7%. This result confirms that the presence of MIM inhibits the formation of conjugated compounds. Finally, the yields in saturated products are low when the yields in conjugated products are high elsewhere for the best yields in alcohol, the saturated products values are around 40%.

2.4. HHM of Linseed Oil by Rh/TEA/MIM Catalytic System: Kinetic Follow-up

As the highest alcohol yield was obtained with the Rh/TEA/MIM catalyst combination (1/1000/220), a kinetic follow-up was also carried out to better understand the course of the reaction (Figure 1b). The key differences, compared to the experiment conducted without MIM, are that (i) there is no formation of conjugates and (ii) the reaction proceeds faster (compare Figure 1a with Figure 1b). The formation of aldehydes starts without an induction period and reaches a maximum at 8 h of reaction time, then the yield of aldehydes decreases over time. Simultaneously, the yields of alcohols and hydrogenated compounds increase. After 31.5 h, the conversion is completed and the yields in aldehydes, alcohols and saturated products are equal to 5.5%, 53.5%, and 41.0%, respectively.

2.5. HHM of Various Substrates

In order to find a better comprehension of the linseed oil behavior, a first series of experiments were carried out with linseed oil and its methyl ester derivatives (in mixture or alone). To study a potential difference in reactivity between the triglyceride structure and the chains alone, linseed oil was trans-esterified in the presence of methanol. The obtained mixture was submitted to HHM reaction conditions with and without MIM. The reactivity of linseed oil and trans-esterified linseed oil (TR Linseed oil) was similar and the addition of MIM always has a positive effect by increasing the alcohols yields and by preventing the formation of conjugated compounds (Table 1; compare entries 1–4). As control experiments, the two first catalytic tests of Table 1 were also conducted without syngas and no change in linseed oil was observed.

To widen the scope of this study, sesame oil was also subjected to Rh/TEA/MIM-catalysed HHM. Indeed, sesame oil contains 42% oleic chains, 40% linoleic chains, and no linolenic chains. Gratifyingly, the yields in alcohol and conjugated products go from 15%/26% to 63%/0% in the absence and in the presence of MIM. So, the same beneficial effect of MIM was highlighted with linseed and sesame oils. The behavior of each chain separately was also evaluated. Experiments were carried out with methyl oleate, methyl linoleate, and methyl linolenate. The yields in alcohols and conjugated products for methyl oleate, methyl linoleate, and methyl linolenate are equal to 99%/no conjugated, 4%/41% and 21%/35% without MIM whereas equal to 92%, 40%/0% and 47%/0% with MIM (Table 1; compare entries 7–12). In the case of methyl linoleate and methyl linolenate, it is clear that the presence of MIM prevents from the formation of conjugated compounds leading to the formation of a stable π-allylic rhodium complex known to slow down reaction rates. Indeed, no conjugated compound was formed and the yields in alcohols are higher. Nevertheless, in the case of monounsaturated

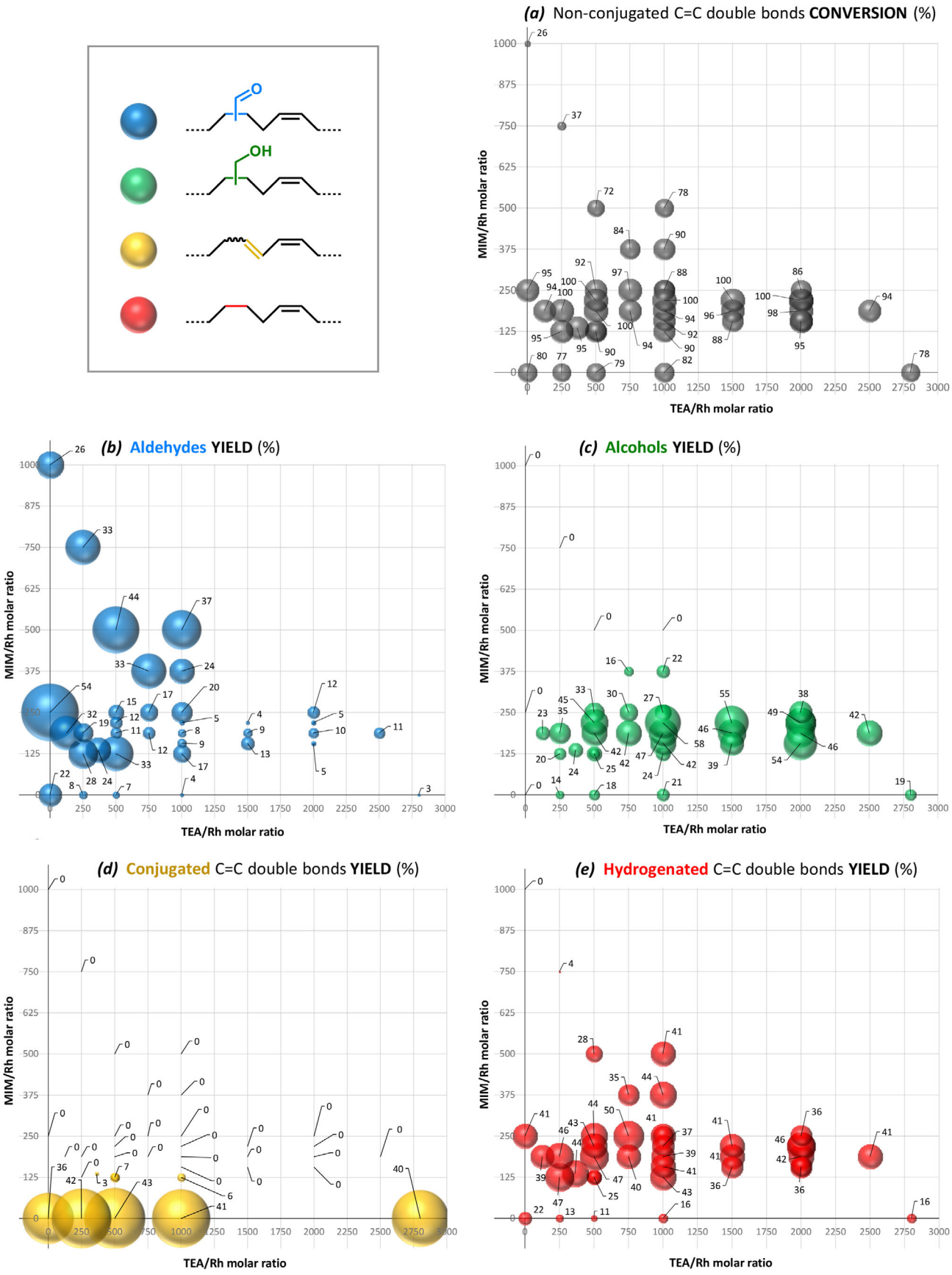


Figure 2. HHM of linseed oil with various ratios of TEA/MIM. Experimental conditions: $Rh(acac)(CO)_2$ (6 mg, 23.3 μmol, 1 equiv), Linseed oil (862 mg, 5.81 mmol, 250 equiv of C=C bonds), Toluene (amount to reach a total volume of 10.2 mL in the autoclave), 80 bar of CO/H_2 (1:1), 80 °C, 24 h.

Table 1. HHM of various substrates.[a)]

Entry	Substrate	Average Number of C=C / Chain (Total in Triglyceride)	Time (h)	MIM / Rh	Conv.[b)] (%)	$Y_{(Ald)}$ [c)] (%)	$Y_{(Alc)}$ [c)] (%)	$Y_{(Conj)}$ [c)] (%)	$Y_{(isomers)}$ [c)] (%)	$Y_{(Sat)}$ [c)] (%)
1	Linseed oil	2.0 (6.0)	24	0	82	4	21	41	–	16
2	Linseed oil	2.0 (6.0)	24	220	100	5	58	0	–	37
3	TR Linseed oil	2.0	24	0	76	5	26	29	–	16
4	TR Linseed oil	2.0	24	220	100	15	50	0	–	35
5	Sesame oil	1.2 (3.5)	24	0	70	19	15	26	–	10
6	Sesame oil	1.2 (3.5)	24	220	95	11	63	0	–	21
7	Methyl oleate	1	24	0	100	0	99	–	–	1
8	Methyl oleate	1	24	220	99	4	92	–	–	3
9	Methyl linoleate	2	24	0	70	17	4	41	–	8
10	Methyl linoleate	2	24	220	100	24	40	0	–	36
11	Methyl linolenate	3	24	0	83	2	21	35	–	25
12	Methyl linolenate	3	24	220	100	6	47	0	–	47
13	Methyl oleate	1	6	0	56	0	53	–	–	3
14	Methyl oleate	1	6	220	28	27	0	–	–	1
15	Methyl 10-undecenoate	1	6	0	100	1	90	–	9	0
16	Methyl 10-undecenoate	1	6	220	88	44	27	–	2	15
17	1-Decene	1	6	0	100	0	95	–	5	0
18	1-Decene	1	6	220	100	61	33	–	1	5

[a)] Experimental conditions: $Rh(acac)(CO)_2$ (6 mg, 23.3 μmol, 1 equiv), TEA (23.3 mmol, 1000 equiv), Substrate (5.81 mmol of C=C bonds, 250 equiv of C=C bonds), toluene (amount to reach a total volume of 10.2 mL in the autoclave), 80 bar of CO/H_2 (1:1), 24 h.
[b)] Non-conjugated C=C double bonds conversion for entries 1–6 and 9–12; C=C double bonds conversion for entries 7–8 and 13–18.
[c)] $Y_{(X)}$ = yield in (X); (Ald) = Aldehydes; (Alc) = Alcohols; (Conj) = conjugated C=C; (isomers) = internal C=C bonds; (Sat) = Saturated=hydrogenated C=C bonds.

substrates, the yields in alcohols (after 6 h) are equal to 53%, 90% and 95% without MIM, whereas with MIM they are 0%, 27%, and 33% for methyl oleate, methyl 10-undecenoate and 1-decene respectively (Table 1; compare entries 13–18). In these cases, the presence of MIM inhibits the activity of the rhodium catalytic species. It seems important to note that in the presence of MIM, C=C isomerisation is reduced (Table 1; compare entries 15–18).

2.6. Origin of the Phenomenon

Since the presence of MIM can have a positive effect by inhibiting the isomerization reaction on the one hand and a negative effect on the functionalization of non-conjugated olefins on the other hand, it seems clear that an interaction between the three partners rhodium, TEA, and MIM takes place. These species would be less active in hydrogenation reaction of the formyl groups and would therefore slow down the reaction. In addition, these species would prevent the isomerization reaction leading to 1,3-diene, thus avoiding the formation of a stable π-allylic rhodium complex and speeding up the reaction. New catalytic species "H[Rh](TEA)(MIM)"-type are probably created. Given that the MIM ligand is less basic than the TEA ligand (pKa=7 instead of 11), the hydrogen atom of these "H[Rh](TEA)(MIM)" species is expected to be less electron-rich than with TEA alone, resulting in a lower hydrogenation capacity towards aldehydes. To support this hypothesis, two experiments using Rh/TEA and Rh/TEA/MIM as catalytic systems were carried out with undecanal as substrate (HHM reaction conditions of Table 1). After 4 h of reaction, the alcohol yields were equal to 100% and 7% in the presence of Rh/TEA and Rh/TEA/MIM, respectively. These two experiments confirmed that Rh/TEA/MIM catalytic system possesses lower hydrogenation capacity towards aldehydes. Furthermore, the less voluminous MIM molecule, compared to TEA, is likely to occupy a vacant site on the "Alkyl-[Rh](TEA)" intermediates, vacant site that a second molecule of triethylamine would have difficulty to coordinate.[37] This capacity would explain that β-elimination is impeded in the presence of MIM, reducing formation of 1,3-dienes and, consequently, of π-allylic complexes. Thus, in the presence of MIM, the classical [Rh/TEA] system becomes more performant in polyunsaturated chains hydrohydroxymethylation.

3. Conclusions

In this work, the reductive hydroformylation of linseed oil and its derivatives was carried out successfully by using a rhodium catalyst precursor associated to TEA and MIM. Generally, the presence of polyunsaturated linoleic and linolenic chains led, by isomerization, to the formation of conjugated systems that strongly inhibits the catalytic system by the formation of a stable π-allylic rhodium complex. Interestingly, in the presence of a precise ratio of TEA/MIM, the isomerization reaction can be inhibited. Control experiments realized on methyl linoleate and methyl linolenate have clearly shown that for the catalytic combination Rh/TEA/MIM, no conjugated products were formed whereas the alcohol yields were increased by a factor 10 and 2.2, respectively. To explain the beneficial effect, spectroscopic studies will be performed to study the new catalytic species involved. As this catalytic system was also efficient for sesame oil, investigations will be carried out to functionalize other challenging vegetable oils containing linoleic and linolenic chains.

4. Experimental Section

All chemicals were purchased from Acros or Aldrich Chemicals and were used without prior purification. Hydroformylation experiments were carried out in a 25 mL (or 100 mL) autoclave (Parr instrument company) equipped with a mechanical stirrer. All runs were performed at least twice to ensure reproducibility. The NMR spectra were recorded at 298 K on a Bruker Avance Neo 400 spectrometer operating at 9.4 T field strength (400 MHz for ^{1}H nuclei and 100 MHz for ^{13}C nuclei) equipped with a 5 mm BBFO SmartProbe (^{1}H/^{19}F/^{31}P-^{109}Ag) and an automatic sample loading system. Chemical shifts are reported in ppm (δ) and were referenced to appropriate internal standards or residual solvent peaks.

In a typical catalytic experiment, a mixture of Rh(acac)$(CO)_2$ (6 mg, 23.3 mmol, 1 eq.), triethylamine (2.35 g, 3.2 mL, 23.2 mmol, 1000 eq.), linseed oil (860 mg, 5.81 mmol, 250 eq. of C=C), *N*-methylimidazole (417 mg, 5.1 mmol, 220 eq.), and toluene (to reach a total volume of 10.2 mL) was transferred into an autoclave of 25 mL (Parr instrument company) equipped with a mechanical stirrer. The autoclave was then heated under stirring and, once a temperature of 80 °C was reached, the autoclave was charged with 80 bar of CO/H_2 (1:1). After 24 h, the autoclave was allowed to cool down to room temperature and depressurized. Triethylamine, MIM, and toluene were removed by rotary evaporator and the obtained mixture was analysed by ^{1}H NMR (Supporting Information).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Hydrohydroxymethylation · Linoleic · Linolenic · Linseed oil · Sesame oil

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