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Amines as Effective Ligands in Iridium-Catalyzed Decarbonylative Dehydration of Biosourced Substrates

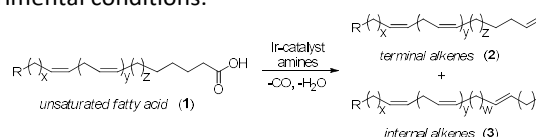
Jérémy Ternel,^a Bastien Léger,^a Eric Monflier,^a and Frédéric Hapiot^{*a}

Linear α -olefins (LAO) and linear internal olefins (LIO) are essential intermediates in the synthesis of surfactants, lubricants, and polymers. Concurrently to petroleum-based industrial processes, the production of LAO and LIO from renewable feedstocks has gained increasing interest in recent years. Organometallic catalysts have been developed designedly, especially Pd, Fe and Ir catalysts. However, such catalysts are mostly stabilized by phosphanes, ligands sometimes difficult to handle especially on large scales. Alternative to phosphanes would thus be highly desirable. In the present study, we demonstrate that Ir catalysts coordinated by amines are suitable to decarbonylate a wide range of biosourced substrates under mild conditions. The resulting LAO and LIO are obtained with good conversion provided that the nature and the quantity of the amine are controlled accurately. The LAO/LIO selectivity can also be tuned by a judicious choice of the experimental conditions. Interestingly, the Ir-based catalytic system is applicable to the decarbonylative dehydration of saturated, unsaturated and polyunsaturated fatty acids.

Introduction

Linear α -olefins (LAO) and linear internal olefins (LIO) have become essential commodity chemicals with a global demand surpassing millions metric tons. Both LAO and LIO can be valorized separately. For example, LAO find application as comonomers for ethylene polymerization, and precursors to plasticizers, lubricants and surfactants that are the basis for shampoos, liquid hand soaps and dishwashing liquids.¹ LIO, for their part, are mainly used as synthetic-based drilling fluids because they form more lubricious layers at the metal surface. Their properties cause them to be used in paper sizing as well. LAO and LIO can also be employed as mixtures containing variable proportions of the two components. For example, automotive manufacturers prefer to use synthetic lubricants over conventional as they contain LIO. Their thermal stability and lubricity help in preventing sludge formation in vehicle engines, thus enhancing fuel efficiency, vehicle performance and equipment life. Mixtures are also preferred in detergents to increase their versatility. From a synthesis viewpoint, the Fischer–Tropsch process,^{2,3,4,5,6,7} and the oligomerization of ethylene^{8,9,10,11,12,13,14} are the most developed processes to synthesize short-chain LAO (C4–C8) while the Shell Higher Olefin Process (SHOP) process leads to long-chain LAO and LIO.¹⁵ A recent publication described the use of a trimetallic catalyst system (Y–Al–Ni) for the tunable synthesis of LAO through coordinative chain-transfer polymerization.¹⁶ LIO are mainly synthesized through LAO isomerization.¹⁷ To overcome the dependence on petro-sourced products, environmentally friendly processes should be developed. In this context, the synthesis of LAO and LIO from renewable resources offers a relevant alternative, both from an environmental and economic point of view. Among renewables, unsaturated long-chain aliphatic carboxylic acids, esters, and triglycerides are of major interest. They constitute an eco-friendly alternative to fossil feedstock as they are derived from vegetable oils and animal fats.¹⁸ Several approaches have been developed to functionalize these molecules by terminal or internal C=C bond. One of them consists in the metathesis (especially ethenolysis) of unsaturated vegetable oils and fatty acid methyl esters (FAME).^{19,20,21,22,23,24,25,26,27,28,29} Another strategy consists in fatty acids decarboxylation.^{30,31} Examples include silica/alumina

catalysts³² or Lewis-acid catalysts³³ for the selective production of LAO by decarboxylation of lactones and unsaturated carboxylic acids. Decarbonylative dehydration of fatty acid to give valuable odd-numbered LAO and LIO olefins has also witnessed increasing interest.³⁴ For example, decarbonylation of heptanoic acid can be achieved over carbon-supported Pt nanoparticles.³⁵ However, turn-over frequencies (TOF) are low because of catalyst deactivation.^{36,37,38} A more recent strategy entails transition metal-catalyzed decarbonylative dehydration of fatty acids. A variety of metals have been shown to catalyze the transformation such as Pd,^{39,40,41,42} Rh,^{43,44} Ni,^{45,46,47} Ir,⁴⁸ and Fe⁴⁹ catalysts. Of interest, combination of Ir-catalyst, Ac₂O and KI allows for a decrease in the temperature reaction and an increase in the product yield. We recently assessed the catalytic performance of Ir catalysts coordinated by phosphanes in the decarbonylation of biosourced unsaturated fatty acids.⁵⁰ The purity of the substrates, the nature of the Ir-coordinated phosphane, and the amounts of the additives (KI and Ac₂O) are key parameters to optimize the catalytic performance. There are, however, a number of problems that are frequently encountered in the use of phosphane ligands. They are air-sensitive and the notorious degradation of P–C bonds can result in deactivation of the catalyst. To get rid of troublesome phosphanes, we recently envisaged the use of the more easy-to-handle amines as ligands. Herein, we demonstrate that unsaturated biosourced fatty acids can be efficiently decarbonylated under relatively mild conditions using Ir catalysts coordinated by amines under homogeneous catalytic conditions (Scheme 1). The studied phosphane-free catalytic system is easy to implement as it proceeds under air atmosphere. The conversion and LAO/LIO selectivity are discussed throughout a detailed optimization of the experimental conditions. Interestingly, it is shown that the LAO/LIO can be precisely tuned by a judicious choice of the experimental conditions.



Scheme 1. Ir-catalyzed decarbonylative dehydration of unsaturated fatty acids.

Results and discussion

Oleic acid (**1a**, 88 wt% purity), which contains only one carbon-carbon double along its alkyl chain, was first chosen as a model substrate to simplify the analysis of the reaction products. [Ir(COD)Cl]₂ (COD = cyclooctadiene) was considered as catalyst precursor, and potassium iodide and acetic anhydride were used as co-reactants (Table 1). Addition of KI causes ligand exchange between Cl and I and exalts the reactivity of the Ir-precursor.⁴⁸ Acetic anhydride, for its part, condenses with oleic acid to form a mixed anhydride. Oxidative addition of the latter on the Ir-precursor gives the acyl iridium complex that undergoes decarbonylation. We performed several catalytic runs to examine the influence of various reaction conditions on both activity and selectivity (Table 1; also see ESI, Table S1 for additional experiments). The formation of the corresponding LAO (**2a**) and LIO (**3a**) was monitored by ¹H NMR spectroscopy (ESI). A blank catalytic test showed that no reaction took place in the presence of [Ir(COD)Cl]₂ without any ligand and additive (Table 1, entry 1), even at higher temperature (ESI, Table S1). Addition of KI led to a poor 12% conversion (entry 2). Decarbonylation reactions were performed under nitrogen. Under air atmosphere, a significant decrease in the conversion was noticed probably because of the formation of peroxides that inhibit the Ir-catalyst (entry 3). Logically, if NPh₃ (considered as the amino equivalent of PPh₃) was added in solution without metallic precursor, no conversion could be detected. Combination of [Ir(COD)Cl]₂ and excess NPh₃ led to an encouraging 42% conversion within 8 h and a rather balanced ratio between terminal and internal olefins (entry 3). Addition of KI greatly improved the catalytic activity as the conversion reached 88% and a higher selectivity in terminal olefins (two thirds of the analyzed products). Note that TEM images recorded from the crude reaction solution clearly showed the absence of Ir-nanoparticles under the chosen catalytic conditions (ESI, Fig. S21). Changing NPh₃ into HNPh₂, a considerably lower conversion was afforded (only 13% conv., entry 5), probably because of side-reaction of the secondary amine with acetic anhydride that led to secondary amides whose coordination ability towards Ir complexes were lower than tertiary amines. Alkylamines also proved to be effective in Ir-catalyzed decarbonylation of **1a** (entries 6-13). However, none of them surpassed NPh₃ whether in terms of catalytic activity or **2a/3a** selectivity, irrespective of their class, and their electronic and steric properties. The best conversion (72%) was measured with *N,N,N'*-TriMe-1,3-PD (entry 10) and the best **2a/3a** selectivity with *N,N'*-TetraMe-1,3-PD (entry 11). Ligands featuring delocalized nitrogen such as DMF (entry 14) or aromatic amines such as pyridine (entries 15 and 16) gave very low conversions. Their too weak σ-donating ability towards Ir probably prevented the formation of an effective Ir catalyst. Accordingly, NPh₃ appears to be the best amine to stabilize Ir catalyst under such experimental conditions. NPh₃ is electronically and sterically suitable to provide a fine balance between (thermodynamic) stability and (catalytic) activity. In terms of catalytic activity, the Ir/NPh₃ combination remained less efficient than the Ir/PPh₃ couple (max. 78% conv. within 8 h vs. 90% conv. within 5 h, respectively).⁵⁰

Table 1. Ligand effect on conversion of **1a** and **2a/3a** selectivity.^a

| Entry | Ligand (mol%) | Additive (mol%) | Conv. ^b (%) | Sel. 2a/3a ^b |
|----------------|---|-----------------|------------------------|--------------------------------|
| 1 | - | - | 0 | - |
| 2 | - | KI (50) | 12 | 50/50 |
| 3 ^c | NPh ₃ (15) | KI (50) | 37 | 58/42 |
| 2 ^d | NPh ₃ (15) | - | 0 | - |
| 3 | NPh ₃ (15) | - | 42 | 45/55 |
| 4 | NPh ₃ (15) | KI (50) | 88 | 61/39 |
| 5 | NHPh ₂ (15) | KI (50) | 13 | 60/40 |
| 6 | NEt ₃ (15) | KI (50) | 28 | 35/65 |
| 7 | ED ^e (15) | KI (50) | 32 | 40/60 |
| 8 | <i>N,N,N'</i> -TriMe-1,2-ED ^e (15) | KI (50) | 61 | 55/45 |
| 9 | <i>N,N</i> -TetraMe-1,2-ED ^e (15) | KI (50) | 15 | 60/40 |
| 10 | <i>N,N,N'</i> -TriMe-1,3-PD ^f (15) | KI (50) | 72 | 56/44 |
| 11 | <i>N,N'</i> -TetraMe-1,3-PD ^f (15) | KI (50) | 64 | 63/37 |
| 12 | Dicyclohexylamine (15) | KI (50) | 30 | 57/43 |
| 13 | Diethylamine (15) | KI (50) | 35 | 45/55 |
| 14 | DMF (15) | KI (50) | 10 | 59/41 |
| 15 | pyridine (15) | KI (50) | <5 | - |
| 16 | 4-dimethylamino-pyridine (15) | KI (50) | 0 | - |

^aReaction conditions: Oleic acid **1a** 88 wt% (1.0 mmol), [Ir(COD)Cl]₂ (0.025 mmol), acetic anhydride (2 mmol), 160 °C, 8 h. ^bDetermined by ¹H NMR spectroscopy. ^cunder air atmosphere. ^dno iridium catalyst. ^eED = ethylenediamine. ^fPD = propylenediamine.

The strong coordinating PPh₃ ligand promotes more stable and more selective Ir catalysts, as anticipated by the HSAB concept.⁵¹ The proportion of LIO is also higher using amines as ligands. While the **2a/3a** ratio is up to 87/13 with the Ir-PPh₃ catalyst, the proportions of LIO can be as high as 65% with the Ir-NEt₃ catalyst (entry 6). Note that, whatever the ligand, the extent of isomerization was limited as only two isomerization products (internal alkenes) could be detected by GLC (ESI, Fig. S19). Also note that a slight variation of the **2a/3a** selectivity was observed over time. For example, using *N,N'*-TetraMe-1,3-PD as amine, it decreased from 69% after 2 h (18% conv.) to 56% after 12 h (99% conv.) (ESI, Table S2).

The conversion and the **2a/3a** selectivity could be optimized by changing the ligand's loading. No conversion was observed using 5 mol% NPh₃, suggesting that a minimum of ligands was required to promote the formation of effective Ir-catalyst (Table 2, entry 1). A similar trend had been found previously with PPh₃ as a ligand.⁵⁰ With 10 mol% NPh₃, the conversion reached 48%

and the products mixture consisted of two third of **2a** and one third of **3a** (entry 2). The best conversion (78%) was measured using 15 mol% NPh₃, with little impact on the **2a/3a** selectivity (entry 3). Further increase in NPh₃ loading up to 30 mol% resulted in a drop in activity (entries 4 and 5). This is not surprising as higher ligand to metal ratio may lead to the blocking of coordination sites, thereby reducing the catalytic activity.

Table 2. Effect of ligand and precursor loading on conversion and **2a/3a** selectivity.^a

| Entry | Ligand (mol%) | Conv. ^b (%) | Sel. ^b 2a/3a |
|-------|-----------------------|---------------------------|-----------------------------------|
| 1 | NPh ₃ (5) | <5 | - |
| 2 | NPh ₃ (10) | 48 | 65/35 |
| 3 | NPh ₃ (15) | 78 | 63/37 |
| 4 | NPh ₃ (20) | 68 | 62/38 |
| 5 | NPh ₃ (30) | 45 | 60/40 |

^aReaction conditions: Oleic acid **1a** 88 wt% (1.0 mmol), [Ir(COD)Cl]₂ (0.025 mmol), acetic anhydride (2 mmol), KI (0.5 mmol), 160 °C, 8 h.^b Determined by ¹H NMR spectroscopy. Accordingly, most of the following catalytic experiments were carried out using an optimal loading of 15 mol% amines.

Catalyst systems derived from NPh₃ did show some sensitivity to the reaction temperature. Less than 5% of **1a** were converted at 120 °C within 8 h (Table 3, entry 1). Raising the temperature to 140 °C resulted in 22% conversion and a **2a/3a** selectivity of 73/27 (entry 2). Increasing the reaction temperature to 160 °C not only speeded up the conversion rate of **1a**, but also promoted the formation of **3a** (entry 3). Further increase in the temperature up to 180 °C turned out to have a beneficial influence on the catalytic activity while the selectivity was dramatically affected (**2a/3a** ratio of 28/72, entry 4). Increasing the reaction time to 16 h allowed full conversion of **1a** mainly into LIO (84%, entry 5). Reducing the ligand loading to 10 mol% slightly altered the conversion and did not modify the **2a/3a** selectivity (entry 6). Substituting NPh₃ by *N,N'*-TetraMe-1,3-PD did not change trends. The effect on the **2a/3a** selectivity was even amplified upon increasing the temperature, as the proportion of isomerized products was greatly enhanced (entries 7-12). Note that *N,N'*-TetraMe-1,3-PD led to the almost exclusive formation of LIO at 180 °C. This is of great interest as pure LIO with a narrow carbon number range are usually produced in small quantities at a great cost. Whatever the amine, conversion and **2a/3a** selectivity varied in opposite directions. Low conversion and large proportion of LAO were obtained at 140 °C while high conversion and large amounts of LIO were measured at 180 °C. It was of interest to see if any difference could be observed in Ir-catalyzed decarbonylation as function of the number and location of the carbon-carbon double bonds along the chain of the carboxylic acids. To this end, we investigated the decarbonylation of various biosourced

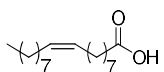
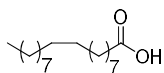
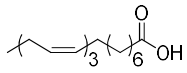
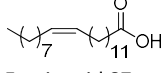
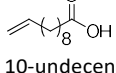
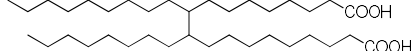
substrates. Only oleic acid reacted to any appreciable extent, affording 99% conversion within 12 h at 160 °C (Table 4, entry 1). The Ir-catalyst turned out to be slightly less active with the saturated counterpart, namely stearic acid without affecting the LAO/LIO selectivity (entry 2). Little difference was seen in decarbonylation of technical linolenic acid (47 wt% pure) in terms of **2c/3c** selectivity (entry 3). The presence of three carbon-carbon double bonds did not disturb the selective pathway during the catalytic cycle as reflected in the constant selectivity found for this system. However, a much reduced activity was observed as the conversion dropped to 66%. The drop in the catalytic activity was likely to be due to, among other reasons, the competitive coordination of unsaturations to the Ir-catalyst, and hence low amount of active sites accessible for catalysis. Compared to oleic acid, lengthening the alkyl chain caused significant decrease in both the conversion and the selectivity. Thus, Ir-catalyzed decarbonylation of erucic acid afforded 86% conversion and a 55/45 selectivity (entry 4). The conversion was moderate for 10-undecenoic acid (only 55%, entry 5). As proposed for linolenic acid, the coordination of the carbon-carbon double bond may be the cause of the reduced catalytic activity. However, in that case, the effect was not limited to the activity as the selectivity was also affected. Actually, balanced proportions of LAO and LIO were obtained. We were also interested in decarbonylating diacids of industrial interest. Commercial Pripol 1012 (building block manufactured by CRODA for coatings, adhesives and engineering plastics) was efficiently decarbonylated producing a balanced 53/47 **2f/3f** ratio. The bifunctional LAO/LIO products may especially find application in polymer chemistry.

Table 3. Effect of temperature on the catalytic performance.^a

| Entry | Ligand (mol%) | Precursor (mol%) | Temp (°C) | Time (h) | Conv. ^b (%) | 2a/3a Sel. ^b |
|-------|----------------------------------|--------------------------------|--------------|-------------|---------------------------|--------------------------------|
| 1 | NPh ₃ (15) | [Ir(COD)Cl] ₂ (2.5) | 120 | 8 | <5 | - |
| 2 | NPh ₃ (15) | [Ir(COD)Cl] ₂ (2.5) | 140 | 8 | 22 | 73/27 |
| 3 | NPh ₃ (15) | [Ir(COD)Cl] ₂ (2.5) | 160 | 8 | 78 | 63/37 |
| 4 | NPh ₃ (15) | [Ir(COD)Cl] ₂ (2.5) | 180 | 8 | 80 | 28/72 |
| 5 | NPh ₃ (15) | [Ir(COD)Cl] ₂ (2.5) | 180 | 16 | 100 | 16/84 |
| 6 | NPh ₃ (10) | [Ir(COD)Cl] ₂ (1) | 180 | 16 | 89 | 15/85 |
| 7 | <i>N,N'</i> -TetraMe-1,3-PD (15) | [Ir(COD)Cl] ₂ (2.5) | 120 | 8 | <5 | - |
| 8 | <i>N,N'</i> -TetraMe-1,3-PD (15) | [Ir(COD)Cl] ₂ (2.5) | 140 | 8 | 20 | 66/34 |
| 9 | <i>N,N'</i> -TetraMe-1,3-PD (15) | [Ir(COD)Cl] ₂ (2.5) | 160 | 8 | 64 | 64/36 |
| 10 | <i>N,N'</i> -TetraMe-1,3-PD (15) | [Ir(COD)Cl] ₂ (2.5) | 180 | 8 | 78 | 26/74 |
| 11 | <i>N,N'</i> -TetraMe-1,3-PD (15) | [Ir(COD)Cl] ₂ (2.5) | 180 | 16 | 100 | 5/95 |
| 12 | <i>N,N'</i> -TetraMe-1,3-PD (10) | [Ir(COD)Cl] ₂ (1) | 180 | 16 | 82 | 6/94 |

^aReaction conditions: Oleic acid **1a** 88 wt% (1.0 mmol), acetic anhydride (2 mmol), KI (0.5 mmol).^b Determined by ¹H NMR spectroscopy.

Table 4. Ir-catalyzed decarbonylation of biosourced fatty acids.^a

| Entry | Substrate | Conversion (%) ^b | 2a-f/3a-f Selectivity ^b |
|----------------|--|-----------------------------|---|
| 1 |  Oleic acid 88 wt% (1a) | 99 | 61/39 |
| 2 |  Stearic acid 98 wt% (1b) | 86 | 60/40 |
| 3 |  Linolenic acid 47 wt% (1c) | 66 | 62/38 |
| 4 |  Erucic acid 87 wt% (1d) | 86 | 55/45 |
| 5 |  10-undecenoic acid 98 wt% (1e) | 55 | 55/45 |
| 6 ^c |  Pripol 1012 (1f) | 72 | 53/47 |

^aReaction conditions: **1a-1e** (1.0 mmol), [Ir(COD)Cl]₂ (0.025 mmol), NPh₃ (0.15 mmol), acetic anhydride (2 mmol), KI (0.5 mmol), 160 °C, 12 h.^b Determined by ¹H NMR spectroscopy.^c **1f** (2.0 mmol), [Ir(COD)Cl]₂ (0.050 mmol), NPh₃ (0.30 mmol), acetic anhydride (4 mmol), KI (1 mmol), 160 °C, 18 h.

Conclusions

To summarize, the present investigation highlights the exciting development of novel Ir-based catalytic systems combining amines and iridium precursors to catalyze the decarbonylation of a wide range of biosourced fatty acids, from saturated to polyunsaturated derivatives. The catalytic system is readily prepared in situ from commercially available and air stable amine and iridium sources, circumventing the need for air-sensitive organometallic complexes. Key parameters are the nature and the amount of amines and the reaction temperature. The reactivities demonstrated here undoubtedly compete with those found for the most active systems that have been recently developed, especially those based on phosphanes. The main advantage of the studied process lies in the tunability of the LAO/LIO selectivity of the Ir-catalyzed decarbonylation reaction. Actually, the proportion of LAO and LIO can be controlled by a relevant choice of the amine and experimental conditions. It should be emphasized that we have found an economically way to orient the decarbonylative dehydration almost exclusively to the formation of LIO. We hope the present article will stimulate and guide future empirical research on the synthesis of LAO and LIO, whether in pure form or blended.

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