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## COMMUNICATION

## Overcoming Rigidity: Flexible aliphatic ligand backbones as a standard for the alkoxy carbonylation of alkenes

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**In this study, we present significant advancement for the palladium catalysed alkoxy carbonylation of aliphatic olefins. A comparison of privileged bidentate phosphines with different ligand backbones was conducted. Therefore it can be inferred that L3, with its propyl backbone, is capable of challenging the state-of-the-art systems (L1, L2). This ligand is particularly well suited for ester synthesis from simple alkenes with industrial relevance and challenging alkenes having internal or multiple double bonds. In comparison with the other tested ligands, L3 facilitates more efficient synthesis and scaling up.**

## Introduction

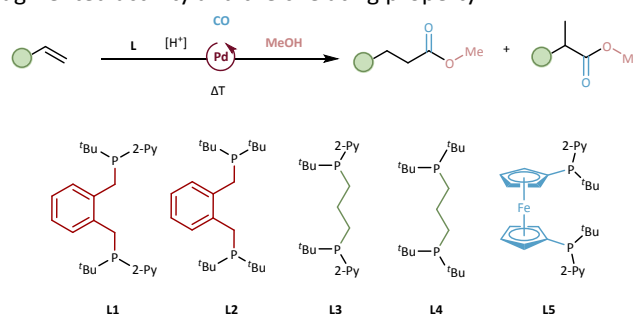
In the domain of homogeneous catalysis, carbonylations catalysed by transition metals are recognised as pivotal reactions within contemporary academic and industrial contexts.<sup>1-4</sup> These reactions enable the transformation of substrates, including alcohols, aryl halides, and olefins, into various products such as acids, aldehydes, amines, and esters.<sup>1, 2, 4, 5</sup> The importance of esters in daily life is underscored by their extensive utilisation in various applications, including solvents, fragrances, and insecticides. Furthermore, esters find application as monomers in polymer synthesis and as building blocks in chemical and pharmaceutical syntheses.<sup>6-16</sup> Given their importance, a broad range of ester syntheses have been developed in recent decades. Nonetheless, investigation in this domain had already commenced prior to the discovery of the Fischer esterification in 1895, in which carboxylic acids and alcohols were converted into esters.<sup>12, 17</sup> Particularly, the alkoxy carbonylation of olefins garnered significant attention owing to its perfect atom economy as all the substrates, the alkene, carbon monoxide (CO), and alcohol are exclusively converted to esters.<sup>5, 6, 8, 18, 19</sup> In this respect, the isomerising alkoxy carbonylation process is of significant industrial relevance, as it enables the selective synthesis of esters from feedstocks comprising both terminal and internal alkenes. Already today, the alkoxy carbonylation is a pivotal industrial

process in the production of methyl propanoate, a crucial precursor for the synthesis of methyl methacrylate (MMA), a highly relevant compound in industrial manufacturing. The Lucite Alpha I-III processes are particularly notable, operating at an annual scale of over 300,000 tons.<sup>13-15, 20-25</sup> The process involves the carbonylation of ethylene, facilitated by a bidentate phosphine ligand, followed by a condensation step with formaldehyde to yield the desired MMA.<sup>14-16, 19-23</sup>

Common alkoxy carbonylation reaction systems employ a phosphine-modified palladium complex, which is activated by an acidic co-catalyst. The modification of the structure of the ligands used, and thus the steric environment of the catalyst, serves as a potent tool for the modulation of selectivity, activity, and the stability of the entire catalytic system.<sup>13, 18, 23, 26, 27</sup>

In the case of bidentate ligands, the variation of the electronic properties and the steric hindrance of the substituents on the phosphorous atoms will also influence the bite angle of the ligands. This phenomenon also directs the outcome of the reaction, as adjustments can be made to control whether branched or linear products are formed.<sup>16, 23, 27, 28</sup>

In addition to selectivity, the electronic properties of substituents can also significantly influence the energy barriers of transition states. As the bite angle (P-M-P) of bidentate phosphine ligands increases, there is a decrease in electron density at the metal center, which favors the nucleophilic attack of the alcohol. Nevertheless, this concurrently diminishes the chelating property of the ligand. Consequently, it is imperative to select ligands with the optimal bite angle to capitalise on the augmented activity and the chelating property.<sup>14, 29</sup>



**Figure 1:** General reaction scheme of the methoxycarbonylation of olefins and a selection of current state-of-the-art ligands chosen for this study.

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In recent decades, specifically 1,2-bis((di-*tert*-butyl-phosphino)methyl)-benzene (Lucite  $\alpha$  ligand, **L2**) has been identified as an outstanding ligand for methoxycarbonylation of olefins. Inspired by this success, a series of derivatives characterised by modified electronic and steric properties of the phosphorus atoms were developed.<sup>16, 20, 21</sup> In this respect, we also introduced a variety of related ligands, including LIKATPhos (**L1**), where one *tert*-butyl group on each side of the Lucite  $\alpha$  ligand is replaced with pyridyl units. A broad array of esters, encompassing saturated and unsaturated monocarboxylic acid esters, as well as dicarboxylic acid diesters, can be obtained through the application of ligands that possess integrated basic sites.<sup>3, 11, 14, 30, 26, 31, 32</sup>

Most variations of the Lucite  $\alpha$  ligand make use of a rigid ligand backbone, a configuration that is regarded more advantageous in comparison to a flexible one.<sup>27, 29</sup> In contrast, the utilisation of more flexible backbones that diverge from the well-known rigid arene core has been less extensively explored. To address this shortcoming, this study uses **L3** to highlight the under-exploited potential of ligands with flexible backbones.

## Results and discussion

In order to compare the known ligands (**L1-L5**)<sup>1, 13, 20, 22</sup> in the isomerising alkoxy carbonylation, the present studies commenced with 1-octene (**1**) as an industrially relevant model substrate. To utilise the full potential of **L3**, which was previously employed using relatively harsh reaction conditions (0.5 mol% Pd precursor, 40 bar CO, 120 °C *p*-TSA as co-catalyst, catalyst:ligand:acid ratio: 1:4:16), we aimed at enabling milder reaction conditions. To highlight differences in performance, the temperature, reaction time as well as the Pd loading was drastically reduced compared to previous work on **L3**<sup>1</sup> (80 °C, 2 hours, 0.04 mol% Pd precursor). Furthermore, CO pressure and the catalyst:ligand:acid ratio were also modified (30 bar CO, 1:4:10). The milder conditions facilitated the discernment of discrepancies in performance and yield of the desired ester (**2**) (Table 1). Under these conditions, a series of ligands with xylene

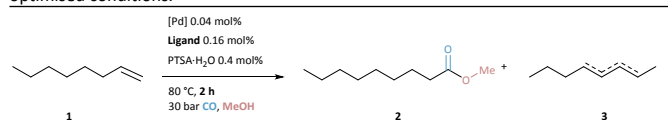
(**L1, L2**), aliphatic (**L3, L4**) and ferrocenyl backbones (**L5**) were tested for comparison (Table 1). Regardless of the diminished reaction time, a comparable octene consumption of greater than 99% is evident for **L1-L3**, and **L5**, attributable to isomerisation and subsequent methoxycarbonylation.

However, significant differences are found comparing the ester yield, the *n*/*iso* ratio, and the amount of remaining C<sub>8</sub> alkenes. A direct comparison of **L3** and **L4** shows improved performance for the former ligand despite the same backbone. Under these conditions, **L3** achieved an ester yield of >80% with a conversion of 99% despite the relatively short reaction time (Table 1, entry 3), with only a small portion of 11% C<sub>8</sub> compounds remaining. This showcases the superior activity of **L3** due to the integrated base moieties enhancing the overall reaction efficiency of the system. The comparison of **L1** and **L5** with **L3**, reveals a significantly lower ester yield for **L1** and **L5** then for **L3**, albeit in all three cases the conversion is >99%. The utilisation of **L2** results in a high conversion of 99%, yet only 10% of the ester is formed. The enhanced outcomes observed with **L3** are presumably attributable to a combination of both the basic pyridine moieties and the more flexible aliphatic backbone.

To illustrate the versatility and improved reactivity of the catalyst system with **L3**, a range of different olefins were investigated, with a special emphasis on industrially relevant starting materials. These include alkenes with internal, terminal, cyclic as well as multiple double bonds. The scope of the study was divided into two sections. In the first section (Section A), industrially relevant substrates were subjected to optimised reaction conditions with a low palladium loading of 0.04 mol%. In the second section (Section B), less reactive substrates were converted using a slightly higher catalyst loading of 0.08 mol%.

As demonstrated in section A, **L3** consistently yields optimal outcomes with minimal catalyst loading, exhibiting a marked preference for the formation of the desired *n*-esters, including methyl hexanoate (**2a**, 63% *n*-ester, TON: 1500) and methyl pentanoate (**2b**, 62% *n*-ester, TON: 2440). Industrially relevant ethylene could be converted to methyl propionate (**2c**) with a turnover number of >100,000 and a particularly low catalyst loading of 9.5 ppm. Substrates that are more sterically demanding, such as diisobutene (**1d**), also resulted in a high yield of **2d** (85%, TON: 2050; prev. lit. TON: 190<sup>1</sup>). It was observed that cyclohexene (**1f**), which is typically characterised by a lower degree of reactivity in comparison to terminal olefins, could be successfully converted to its corresponding ester (**2f**), showing a remarkable yield of 90% (TON: 2250). Finally, neohexene (**1e**) could also be successfully transformed into the corresponding methyl ester (**2e**) in a yield of 65% (TON: 1625). In section B, the catalyst loading was increased to facilitate the conversion of more challenging substrates to their corresponding esters. These include substrates with steric hindrance, functional groups and internal double bonds, as well as substrates with multiple double bonds.

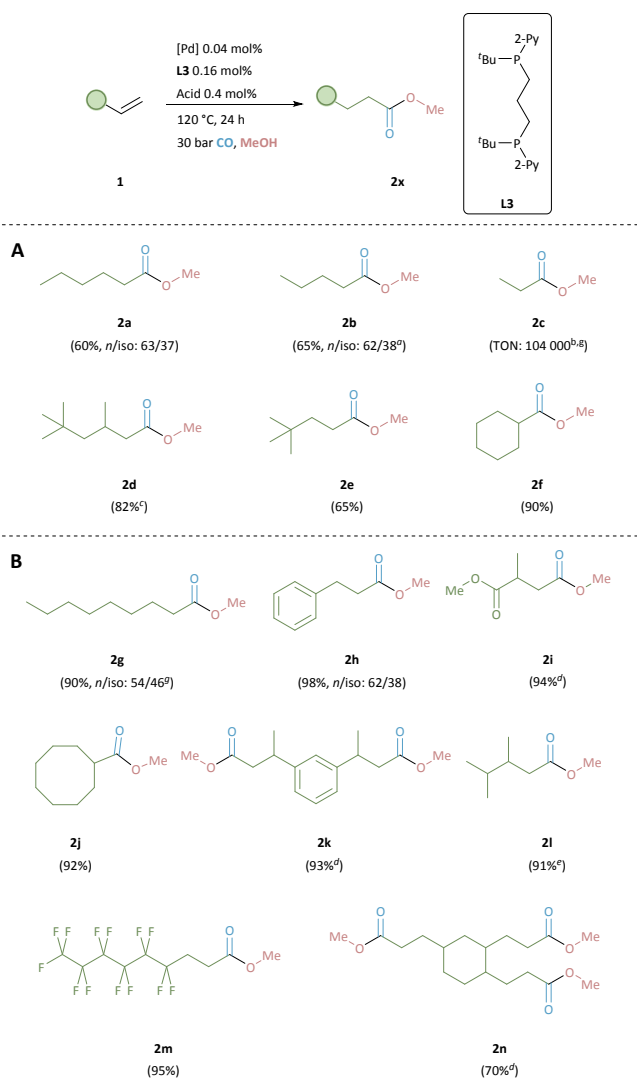
**Table 1:** Screening of different ligands for the alkoxy carbonylation of 1-octene using optimised conditions.<sup>a</sup>



Entry	Lig.	Conv. <sup>c</sup> [%]	Σ Esters [%]	<i>n</i> / <i>iso</i> [%]	<b>3</b> <sup>d</sup> [%]
1	<b>L1</b>	>99	76	76/24	17
2	<b>L2</b>	99	10	94/06	81
3	<b>L3<sup>b</sup></b>	99	82	59/41	11
4	<b>L4</b>	9	-	-	1
5	<b>L5</b>	>99	60	60/40	34

<sup>a</sup>conditions: **1** (20 mmol), Pd(acac)<sub>2</sub> (0.008 mmol), Ligand (0.032 mmol), PTSA-H<sub>2</sub>O (0.08 mmol), MeOH (20 mL), CO (30 bar), 80 °C, 2 h. <sup>b</sup>The ligand was synthesised using a different synthesis route (see supporting information for details). <sup>c</sup>remaining C<sub>8</sub> alkenes including 1-octene. <sup>d</sup>The conversion, the *n*/*iso* ratio and the amount of remaining C<sub>8</sub> alkenes were determined using mesitylene as the internal standard.

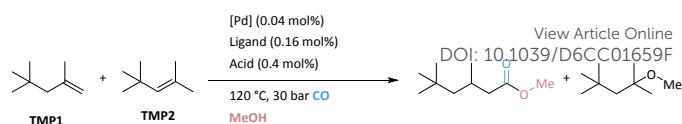




**Figure 2:** Palladium-catalysed alkoxy carbonylation of olefins: substrate scope.

Conditions **A**: **1** (20 mmol), Pd(acac)<sub>2</sub> (0.04 mol%), **L3** (0.16 mol%), PTSA·H<sub>2</sub>O (0.4 mol%), MeOH (20 mL), CO (30 bar), 120 °C, 24 h, isolated yields, *n*/*iso* selectivity determined by GC analysis, <sup>a</sup>60 mmol, <sup>b</sup>682 mmol, 0.00096/ 0.0138/ 0.069 mol% [Pd]/L3/H<sup>+</sup>, <sup>c</sup>80 mmol. Conditions **B**: **1** (20 mmol), Pd(acac)<sub>2</sub> (0.08 mol%), **L3** (0.32 mol%), PTSA·H<sub>2</sub>O (0.8 mol%), MeOH (20 mL), CO (30 bar), 120 °C, 24 h, isolated yields, *n*/*iso* selectivity determined by GC analysis <sup>a</sup>40 mmol, <sup>c</sup>80 °C, <sup>d</sup>0.8/ 3.2/ 8.0 mol% [Pd]/L3/H<sup>+</sup>, <sup>e</sup>yield determined by GC analysis by adding the internal standard mesitylene.

Under these conditions, comparable results are achieved with the isomerising substrate 2-octene (**1g**) as with 1-octene, with nearly identical *n*/*iso* selectivities (*n*/*iso* selectivity of 54/46 compared to 57/43 in Table 4 in the supporting information; TON: 1150). The substrates styrene (**1h**) and MMA (**1i**), which are widely used in industry, are also included in this scope and could both be converted into their methyl esters with excellent yields (**2h**: 98%, TON: 1225; **2i**: 94%, TON: 1163). Cyclooctene **1j**, which contains an internal double bond and is typically considered to be largely unreactive, gratifyingly yielded **2j** with an impressive yield of 92% (TON: 1150; prev. lit. TON: 196<sup>1</sup>). The perfluorinated compound **1m** underwent a transformation into the methyl ester (**2m**; TON: 1188) with a quantitative yield of 95% and the challenging, sterically hindered substrate (**1l**) was isolated with an impressive yield of 91% (TON: 1140).

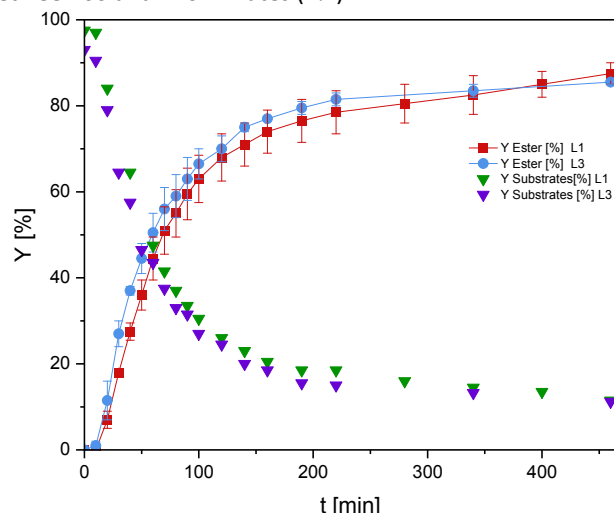


**Figure 3:** Palladium-catalysed methoxycarbonylation of diisobutene with **L1** and **L3**.

Reaction conditions: diisobutene (80 mmol), Pd(acac)<sub>2</sub> (9.75 mg, 0.04 mol%), **L** (0.16 mol%), PTSA·H<sub>2</sub>O (0.4 mol%), MeOH (80 mL), CO (30 bar), 120 °C, 24 h.

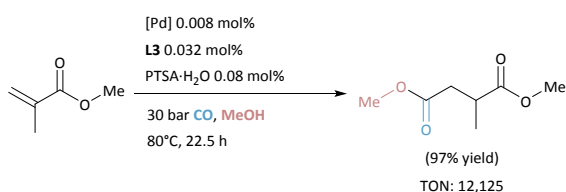
A notable challenge arises in the context of methoxycarbonylations conducted on substrates bearing multiple double bonds. In such cases many competing side reactions (like polymerisations/ telomerisation) can occur and the chemo- and regioselectivity control are particularly difficult. Nevertheless, for 1,3-diisopropenylbenzene (**1k**) we were able to isolate 93% of the desired double-carbonylated product without increasing the catalyst loading (**2k**; TON: 1163; prev. lit. TON: 198<sup>1</sup>). Gratifyingly, in case of highly challenging substrate **1n**, the corresponding triester (**2n**; TON: 875) was isolated in high yield (70%) avoiding mostly the acid-catalysed aromatisation as side reaction.

The use of diisobutene as starting material is of significance within industrial contexts. Here, the objective was to demonstrate that **L3**, with its propyl backbone and simpler synthesis, can hold its own against the widely recognised ligand **L1**. This substrate's distinctive characteristic is its composition, which consists of a mixture of isomers (**Figure 3**). The mixture is predominantly terminal (80%, TMP1), and it also contains a certain amount of internal isomer (20%, TMP2). **Figure 4** compares **L1** and **L3** in the methoxycarbonylation of diisobutene (For the diagrams showing all reaction components, see the supporting information **Figure 2** and **Figure 3**). In the case of **L3**, the formation of the corresponding ester proceeded slightly faster in the first 110 minutes compared to **L1**; from this point onwards, the ester production of **L1** increased compared to **L3**. The ether byproduct is observed only in traces in both cases; peak values can be observed for **L1** between 70 and 160 minutes (3%) and for **L3** between 60 and 120 minutes (2%).



**Figure 4:** Comparison of palladium-catalysed methoxycarbonylation of diisobutene with **L1** and **L3**.





**Figure 5:** Palladium-catalysed methoxycarbonylation of MMA with **L3**. Reaction conditions: MMA (200 mmol), Pd(acac)<sub>2</sub> (4.87 mg), **L3** (23.96 mmol), PTSA·H<sub>2</sub>O (30.44 mmol), MeOH (200 mL), CO (30 bar), 80 °C, 22.5 h.

A comparative analysis reveals that both ligands demonstrate comparable performance within a similar range. It has been demonstrated that both processes result in the conversion of TMP2 to TMP1 with high efficiency, leading to the quantitative production of the desired ester. The outcomes of the reactions after 24 hours appear almost identical. In the case of **L1**, the yield of the corresponding ester is > 98%, whereas the yield with **L3** is 96% after 24 hours. This finding suggests the hypothesis that **L1** and **L3** may engage in analogous activities during the synthesis of the desired product over extended periods. However, **L3** exhibited slightly superior isomerisation catalyst properties. Therefore, **L3** can compete with established ligands such as **L1** and can achieve similarly good results with a simpler ligand synthesis. To demonstrate the industrial relevance, scalability and efficiency of **L3**, MMA was selected as the substrate for scale-up experiments. To achieve this, the reaction was scaled up from 40 to 200 mmol and the Pd loading was reduced from 0.08 to 0.008 mol%. At a ratio of [Pd]/**L3**/H<sup>+</sup> of 1:4:10 under mild reaction conditions (**Figure 4**) methyl 2-methylsuccinate was formed in quantitative yield.

## Conclusion

We have demonstrated that the previously described ligand **L3**<sup>1</sup>, despite its simplified synthesis compared to the more rigid **L1**, represents a highly robust and industrially relevant ligand for the methoxycarbonylation of alkenes. Our results challenge the conventional "rigidity dogma" in carbonylation catalysis; we show that the inherent flexibility of the **L3** scaffold does not compromise selectivity but instead facilitates rapid initiation and high catalytic productivity. Notably, **L3** achieves a six-fold increase in turnover numbers compared to previous benchmarks, maintaining exceptional activity at very low catalyst loadings. The kinetic profiles reveal that **L3** exhibits a significantly shorter induction period than **L1**, reaching near-quantitative yields with an initial rate increase of roughly 20%. This combination of high atom economy, enhanced TON, and synthetic accessibility positions **L3** not merely as a practical alternative, but as a new performance standard for isomerising alkoxy carbonylation. We anticipate that these findings will shift the focus toward optimising conformational flexibility in the design of next generation ligands for large-scale sustainable catalysis.

## Author contributions

H.F. performed the optimisation of the reaction conditions, as well as the reaction scope experiments. The isolation of the products of the reaction scope was carried out by H.F. with the help of R.J. and J.T. H.F. and R.J. synthesised the ligands. J.M. supported H.F. in the synthesis optimisation of **L3**. J.M. and H.F. carried out the experiments for the kinetic investigation. R.J., R.F., and M.B. conceptualised the work. The manuscript was written through contributions from H.F., J.M., J.T., R.J., R.F. and M.B. All authors have approved the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the Supplementary Information (SI). Supplementary information: synthesis and characterisation details of compounds and NMR spectra.

## Acknowledgements

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### Data availability

The data supporting this article have been included as part of the Supplementary Information (SI). Supplementary information: synthesis and characterisation details of compounds and NMR spectra.

