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Development of highly efficient and selective palladium catalysts for telomerization of 1,3-butadiene with alcohols†

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Novel phosphine ligands based on (benzo)furylphosphines, enable the efficient palladium-catalyzed telomerization of 1,3-butadiene with methanol. The synthesis of industrially relevant 1-methoxy-2,7-octadiene (1-MODE) occurs in quantitative yields and excellent productivity (TON = 95.000), even at ambient temperatures.

1-Octene plays a pivotal role in industrial chemistry, with a multi-100 000-ton scale utilization as a monomer in the production of linear low-density polyethylene. Its significance extends to its role as a precursor for plasticizers, alcohols, and solvents, as well as in the production of fine chemicals, including corrosion inhibitors and herbicides.[1,2] Consequently, the synthesis of 1-octene has been a subject of interest for decades, and numerous methods have been developed to achieve this objective, including oligo-merization of ethylene.[3,4] Among the industrial processes that have been applied, telomerization of 1,3-butadiene is noteworthy for its selectivity and environmental friendliness, exhibiting 100% atomic efficiency.[1,5–7]

The telomerization of 1,3-butadiene with methanol was first reported in 1967 independently by Smutny at Shell[8] and Takahashi at Osaka University.[9] In general, the telomerization can selectively afford 1-octene from inexpensive feedstocks through a three-step process (Scheme 1). Initially, the telomer 1-methoxy-2,7-octadiene (1-MODE, **2**) is produced *via* a palladium-catalyzed reaction. It is noteworthy that this step, apart from yielding the desired linear product (1-MODE), can also result in the formation of the branched product (3-MODE) and other byproducts. In the second step, hydrogenation of 1-MODE **2** furnishes 1-methoxyoctane **3**, which subsequently gives 1-octene **4** and methanol by thermal

cracking.[1] The subsequent steps, namely hydrogenation and thermal cracking, are well-established processes that yield their respective products in a quantitative yield. Therefore, the efficiency of the overall process is determined by the telomerization reaction. Consequently, numerous researchers in both industry and academia have demonstrated a persistent interest in this transformation, with the objective of enhancing the yield, catalyst productivity, and selectivity for 1-MODE **2** synthesis.[10–17] To achieve high catalyst activity and regio- and chemoselectivity, a multitude of ligands, particularly mono- and bidentate phosphines, have been developed and evaluated in this transformation over the years.

As an example, in the presence of PPh₃, 1-MODE **2** is obtained in moderate to good yield, but poor linear/branched selectivity.[18–21] Derivatives of PPh₃ containing electron-donating methoxy substituents, especially in the *para* position, have been shown to yield superior results.[22–24] Intriguingly, ligands possessing bulky xanthene backbones have been observed to exhibit remarkable activity at low temperatures, and their oxygen coordination properties have been postulated to contribute to their enhanced performance.[25–27]

In addition, several trialkylphosphines were applied in the conversion of 1,3-butadiene into 1-MODE. It was observed that PEt₃ gave higher selectivity than PPh₃, while PCy₃ tended to give mainly undesired 1,3,7-octatriene instead of 1-MODE **2**.[23,28] Compared to PPh₃, bidentate phosphines showed better selectivity in the telomerization of 1,3-butadiene at lower temperature. Finally, it is worth mentioning that in the past two decades N-heterocyclic carbenes (NHCs) were introduced and studied in detail. These Pd–NHC-complexes afforded 1-MODE **2** in high selectivity in the presence of only ppm amounts of Pd (Scheme 1).[2]

While most prior research has been conducted with *in situ* generated Pd catalysts, some molecularly defined Pd complexes have also been examined in the telomerization reaction. Despite the necessity for additional synthesis steps and the potential increased sensitivity of the corresponding complexes,

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† Electronic supplementary information (ESI) available: CCDC 2339359. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5cc01036e

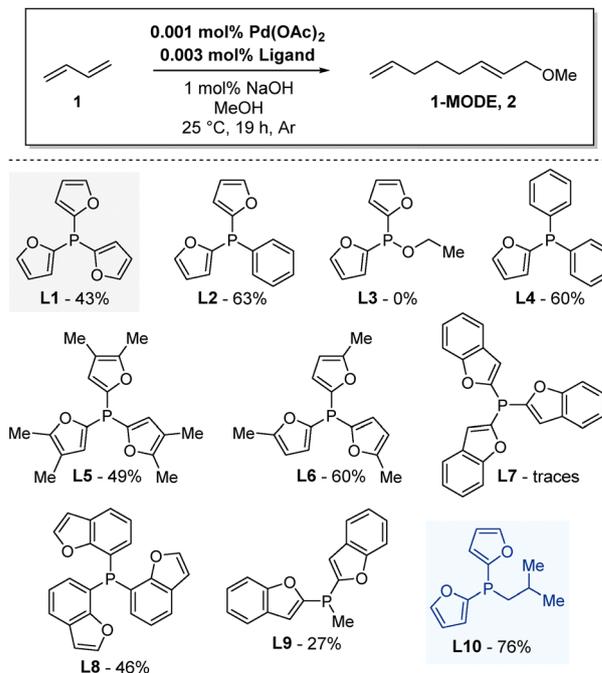‡ These authors contributed equally to the development of this work.
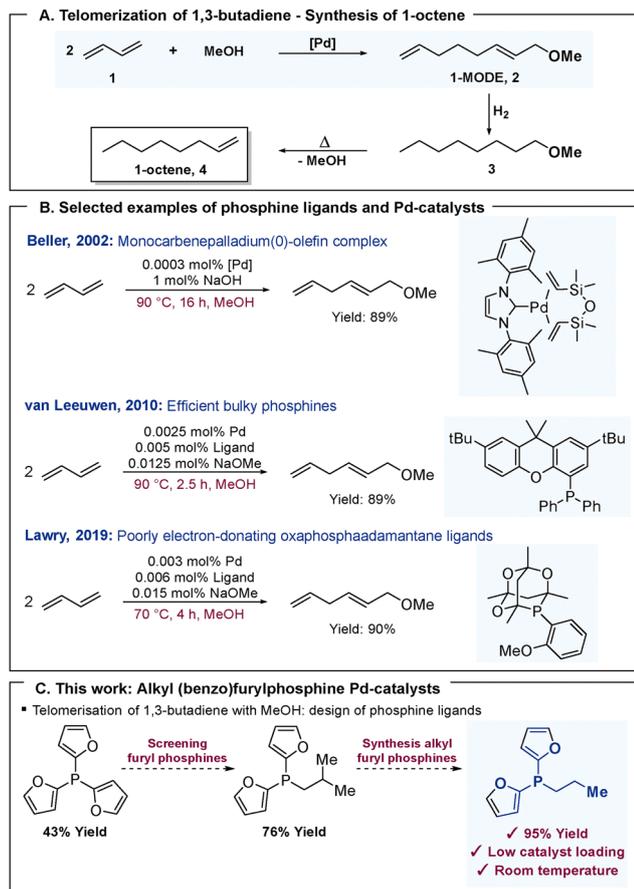
Scheme 1 (A) Synthesis of 1-octene **4** via Pd-catalyzed telomerization of 1,3-butadiene **1** with methanol. (B) Selected examples of ligands and Pd-complexes applied in the synthesis of 1-MODE **2**. (C) Design of alkyl (benzo)furylphosphine ligands for Pd-catalysts.

Table 1 Pd-catalyzed telomerization of 1,3-butadiene with methanol: testing different ligands[a]

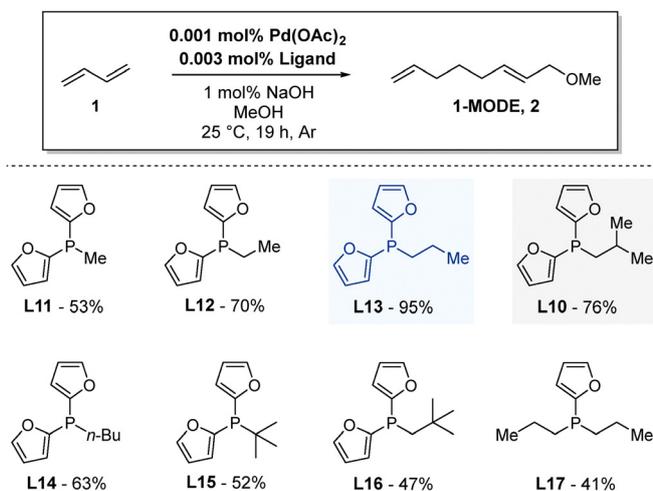[a] Reaction conditions: Pd(OAc)$_2$ (0.001 mol%), ligand (0.003 mol%), NaOH (1 mol%), MeOH (1.5 mL/1.0 g 1,3-butadiene), condensed 1,3-butadiene, Ar, 25 °C, stirring at 750 rpm, 19 h. Yields calculated from GC-FID slope with isooctane as ISTD.

well-defined complex structures offer a distinct advantage in terms of enhanced catalyst activity. For instance, PPh$_3$–Pd–(η^2–η^2-allylether) was shown to be active even at −10 °C.[2,29,30]

Recently, our group prepared novel electron-rich furyl and benzofuryl phosphines for cobalt-catalyzed isomerization reactions. Building upon the above-mentioned previous works in the field of telomerization, we have postulated that the corresponding palladium complexes should be active in this transformation. Consequently, we have initiated a project to evaluate their performance. To enable proper activity evaluation and potential applications, all catalytic experiments were performed at low temperature (room temperature) and low Pd loading (0.001 mol%). Mechanistic studies showed that the active Pd species contains only one coordinated phosphine.[19,31,32] However, to ensure proper stabilization of the active metal species at low metal concentration, a metal : ligand ratio of 1 : 3 was applied. Utilizing PPh$_3$ as a ligand under these conditions gave 1-MODE **2** in 50% yield. In comparison, the use of tri(furan-2-yl)phosphine (TFP) **L1**, a commercially available ligand, resulted in 1-MODE **2**, albeit with a slightly lower yield (Table 1). It is also noteworthy that the majority of the previously examined monodentate ligands are symmetrical in nature. Interestingly, non-symmetric

phosphine, obtained through the substitution of one or two phenyl groups with furyl groups, resulted in the telomerization product **2** in higher yields (**L2**, 60% and **L4**, 63%, respectively). In contrast, the more electron-rich TFP derivatives **L5** and **L6** provided 1-MODE **2** with yields of 49% and 60%, respectively. The evaluation of different tribenzofurylphosphines (**L7–L9**) demonstrated that the resulting orientation of the furan and benzofuran ring plays a crucial role in the coordination to the metal center, which is decisive for the catalytic activity.

While only traces of the desired product were observed with tri-2-benzofuranephosphine **L7**, tri-8-benzofuranephosphine **L8** gave a yield of 46% of 1-MODE **2**. Furthermore, we tested alkyl-substituted furyl and benzofurylphosphines and difuryl-isobutylphosphine **L10** provided the desired 1-MODE **2** in 76% yield. It is noteworthy that most of the catalytic experiments were performed at least twice and exhibited a very good degree of reproducibility. Considering the favorable outcome observed with **L10**, a systematic variation of the alkyl substituent on the difuryl phosphines was employed to enhance the activity of the respective palladium catalyst. A total of eight distinct alkyl difuryl phosphines were synthesized and utilized in the benchmark reaction (see Table 2 for details). The catalysis with the methyl-substituted phosphine **L11** furnished 1-MODE **2** in 53% yield, while the ethyl-substituted ligand **L12** yielded 70% of the product. Notably, the n-propyl-substituted difuryl phosphine **L13** achieved a remarkable 95% yield. Conversely, when iso-butyl-(**L10**) and n-butyl- (**L14**) substituted phosphines were utilized, the

Table 2 Testing di-furyl alkyl phosphines in the Pd-catalyzed telomerization reaction: variation of the alkyl chain length of the ligand[a]

[a] Reaction conditions: Pd(OAc)$_2$ (0.001 mol%), ligand (0.003 mol%), NaOH (1 mol%), MeOH (1.5 mL/1.0 g butadiene), condensed 1,3-butadiene, Ar, 25 °C, stirring at 750 rpm, 19 h. Yields calculated from GC-FID slope with isooctane as ISTD.
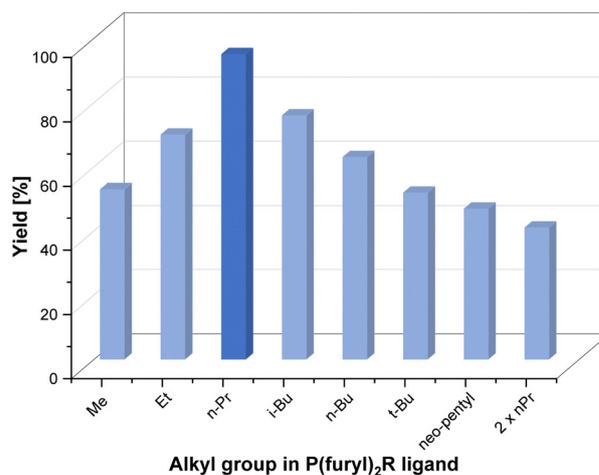
yields were found to be considerably lower, at 76% and 63%, respectively. Ligands bearing alkyl groups with increased steric hindrance, such as *tert*-butyl **L15** and neopentyl **L16**, yielded 1-MODE in 52% and 47% yield, respectively. In the possession of the optimal ligand (**L13**), we proceeded to synthesize **L17**, which possess a single furyl group and two *n*-propyl chains attached to the phosphorus atom. When the telomerization reaction was performed with **L18**, the desired product was obtained in 41% yield, indicating the crucial role of the two furyl motifs and the propyl chain for the activity of the Pd catalyst.

As demonstrated in Table 2, a clear correlation exists between the size of the linear alkyl chain in the ligand and the yield of 1-MODE **2**, which attains an optimal level with *n*-propyl chains. Further increases in chain length ($>n$-propyl) and/or the bulkiness of the alkyl chains result in a decline in the desired product yield. It is noteworthy that the reaction in the presence of difuryl-alkyl-phosphine ligands proceeds with low catalyst loadings at room temperature towards the desired product with high selectivity, yielding exclusively the *Z*-isomer of 1-MODE **2**.

Nevertheless, even more active ligands could be expected by the proper combination of phosphine substituents, *e.g.* **L13** with methyl-furyl units.[33] Even though the yield of 1-MODE **2** was nearly quantitative with **L13** (95%, TON 95.000), further investigation was conducted into the role of the ligand (Table 3). In the absence of a ligand, no product was formed (Table 3, entry 1). Subsequent assessment of the ligand-to-metal ratio (L : M ratio) revealed a decline in yield for 1-MODE **2** when the L : M ratio was 1 : 1 or 5 : 1 (Table 3, entries 2 and 3). Furthermore, the effect of temperature on the telomerization reaction was investigated, and the catalytic system demonstrated optimal efficiency at 25 °C (Table 3, entry 5). Conversely, at 0 °C, the reaction yield was 10% (Table 3, entry 4). At 50 °C, the catalytic system exhibited a 93% yield. However, at elevated temperatures of 70 °C or 90 °C, the yield of 1-MODE 2 decreased to 52% and 58%, respectively (Table 3, entries 6–8). Notably, utilizing only 0.0005 mol% of

Table 3 Pd-catalyzed telomerization: influence of selected reaction parameters[a]

Entry	Changes from standard conditions	1-MODE (%)
1[b]	Without **L13**	0
2	0.001 mol% **L13**	50
3	0.005 mol% **L13**	42
4	0 °C	10
5	25 °C	95
6	50 °C	93
7	70 °C	52
8	90 °C	58
9[c]	0.0005 mol% Pd(OAc)$_2$	35

[a] Reaction conditions: Pd(OAc)$_2$ (0.001 mol%), L13 (0.003 mol%), NaOH (1 mol%), MeOH (1.5 mL/1.0 g 1,3-butadiene), condensed 1,3-butadiene, Ar, 25 °C, stirring at 750 rpm, 19 h. Yields calculated from GC-FID slope with isooctane as ISTD. [b] Reaction performed at 90 °C. [c] Ligand: 0.0015 mol% L13.

Pd(OAc)$_2$ produced the desired product in a moderate yield of 35%, as shown in Table 3, entry 9. Additionally, we investigated the air stability of **L13** and, to our surprise, the electron-rich phosphine **L13** (^{31}P NMR: −62.0 ppm) is considerably stable under aerobic conditions. More specifically, only 6% of the corresponding phosphine oxide **L18** (^{31}P NMR: 12.2 ppm, 1.0 : 0.06 ligand : ligand oxide ratio) was detected in a ^{31}P NMR spectrum after exposing **L13** to air at room temperature for an overnight period.

Following a week of storage in ambient air, the presence of approximately 21% phosphine oxide **L18** (with a ligand : ligand oxide ratio of 1.0 : 0.27) was ascertained through ^{31}P NMR analysis. The complete oxidation of **L13** to **L18** was only achieved using hydrogen peroxide as the oxidizing agent (for

the crystal structure of **L18** see Fig. S4, ESI†). Notably, negligible amounts of 1-MODE **2** were observed with **L18**.

In the previous studies of telomerization reactions, the reactivity of the alcohol was often neglected. To examine the activity of this newly developed catalytic system towards different alcohols, the telomerization reaction was performed in a mixture of two alcohols with very similar structure and properties, namely methanol and ethanol. Notably, under standard conditions (Table 3), the catalytic system demonstrated a high degree of selectivity for methanol, yielding the products 1-MODE : 1-EtODE in a 10 : 1 ratio (ESI†). We assume that this selectivity is a result of the preferred protonation of the Pd–(η^3,η^1-octadienediyl)-complex, formed by the oxidative addition of 1,3-butadiene to the Pd(0)-complex. Notably, even when the percentage of ethanol in the solvent mixture was increased to a 1 : 1 ratio of methanol : ethanol, the reaction remained selective towards 1-MODE (ESI†). This observation led to the subsequent evaluation of the selectivity of the novel catalytic system for methanol in the presence of n-butanol. The resultant 1-MODE : 1-nBuODE ratio of 9 : 1 (ESI†) indicates the high degree of chemoselectivity of this system, which might be used for selective telomerizations of alcohol mixtures and substrates with more than one hydroxyl group. Finally, the mechanism of this reaction is believed to operate in a manner consistent with the findings of the original studies conducted by Jolly and colleagues[31] and subsequent investigations.[32,34–36]

In summary, we have synthesized and applied novel difuryl-alkyl-phosphines for the Pd-catalyzed telomerization reaction of 1,3-butadiene. Notably, the n-propyl derivative (**L13**) was identified as the optimal ligand for the synthesis of 1-MODE **2**. The newly developed catalytic system, as outlined in this report, enables the efficient synthesis of 1-MODE **2** with a high degree of purity using only 0.001 mol% of Pd at ambient temperature. Furthermore, experiments employing mixtures of alcohols in the telomerization reaction demonstrated a high degree of chemoselectivity for the optimal catalyst system.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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