

Palladium-Catalyzed Telomerization of Isoprene with Amines: Ligands and Solvents Working Together to Improve the Selectivity

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Controlling the selectivity in palladium-catalyzed telomerization of nonsymmetric dienes represents a challenge as several isomers can be obtained, although the four resulting from the attack of the nucleophile at the terminal carbon atom are the main products. Concerning telomerization of isoprene using amines as nucleophiles, the selectivity for three of these four isomers, tail-to-head, head-to-head, and tail-to-tail (1–3), were previously optimized as a result of solvent (pKa) and ligand control. However, the head-to-tail telomer (4) was always obtained in low selectivity. In this paper, we test different Pd catalytic systems with phosphine, phosphite, and phosphoramidite lig-

ands under different solvents and pKa conditions to improve the selectivity for telomers 3 and 4. Results showed that, in the telomerization of isoprene with diethyl amine using non-protic solvents and phosphite ligands with large cone angle afforded telomer 3 in high yield and selectivity (up to 90% yield and 90% selectivity for 3). Phosphite ligands with small cone angle provided telomer 4 with selectivity of 43% (80% yield), which was raised to 48% (23% yield) with ^tPr₂NH as nucleophile. The significant effect of residual water on the solvent was quantitatively accessed, and greener solvents were tested as alternative for this reaction.

1. Introduction

The telomerization of dienes is a transition metal-catalyzed reaction known since 1967^[1] that consists in the dimerization of a diene catalyzed by a transition metal, mainly palladium, with subsequent addition of a nucleophile, such as an alcohol, an amine, an acid, or water.^[2] Recently, aryl groups were introduced using boronic acids,^[3] and using nickel catalysts.^[4] Today, buta-

diene telomerization with methanol is the key reaction for the industrial production of 1-octene.^[5]

Telomerization of butadiene, the typical benchmark substrate, can afford three different products, linear or branched resulting from the attack of the nucleophile to Pd- π -allyl intermediate, and a triene resulting from the elimination reaction (Scheme 1). The linear telomer is the major one and is the target for industrial applications. The mechanism for Pd-catalyzed butadiene telomerization^[6] was experimentally confirmed and further described by DFT calculations using methanol and dimethylamine as base.^[7] For asymmetrically substituted dienes, the scenario is much more complex and challenging. Thus, for isoprene, the simplest nonsymmetric diene, the telomerization process can yield several diene isomers resulting from different C—C coupling of the isoprene units, from E/Z isomerism and from the nucleophilic attack at the position 1 or 3 in the carbon chain, as well as the corresponding trienes (without nucleophile incorporation in the carbon chain).

Since the discovery of telomerization reaction, few catalytic systems providing good selectivity in isoprene telomerization with amines have been described (Scheme 2A),^[8–10] and factors responsible for controlling the selectivity were not clearly identified and became controversial. Recently, we reported the selective synthesis of three of four linear telomers that can be obtained in isoprene telomerization with diethyl amine (Scheme 2B), and established the factors responsible for controlling the selectivity, which allowed us to draw a general picture of the isoprene telomerization mechanism.^[11] Based on DFT calculations and kinetic simulations, we proposed the mechanism illustrated in Scheme 3, in which protic solvents and water impurities act as cocatalyst, identifying four main steps: 1) isoprene

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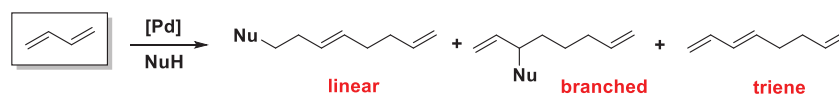
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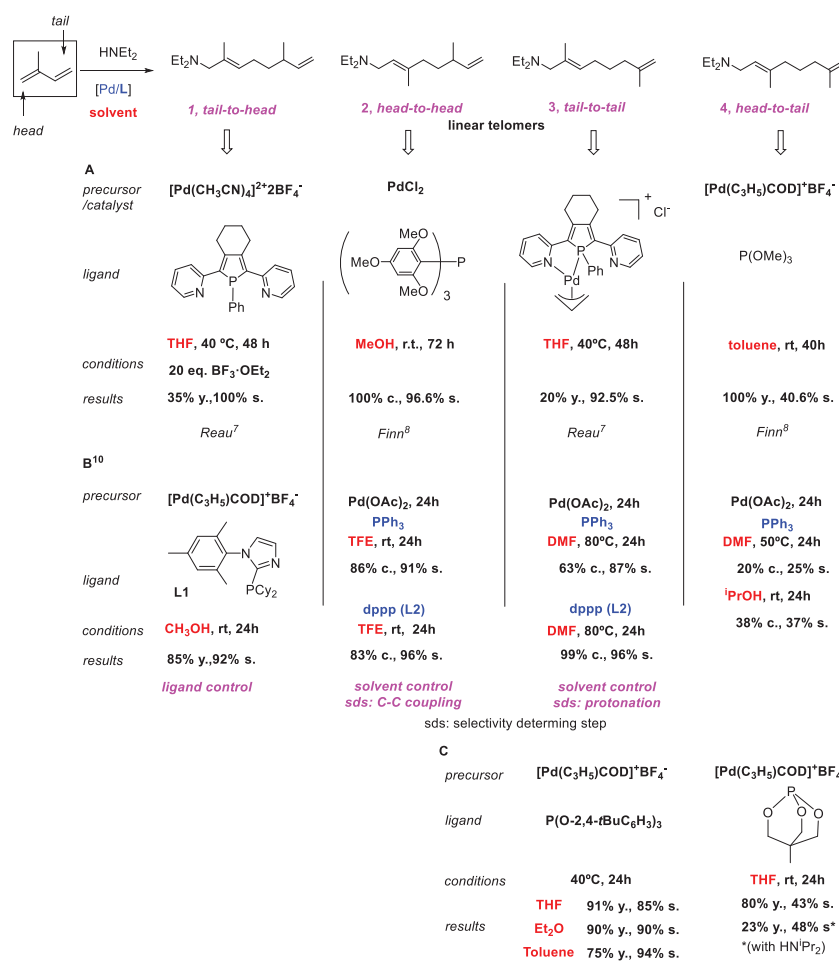
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Scheme 1. Products formed in butadiene telomerization.

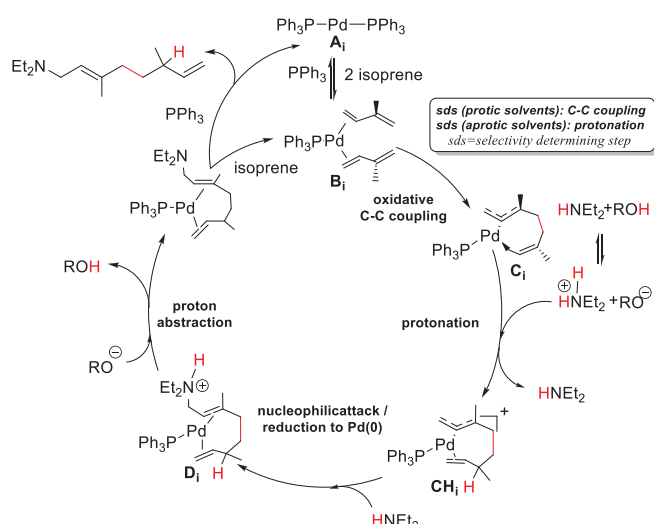
Scheme 2. Yield and selectivity in Pd-catalyzed isoprene telomerization using Et_2NH as nucleophile (selectivity corresponds to the telomer at the top of the column). (A) Selected results from literature. (B) Best results obtained previously in our group. (C) This work.

coordination and oxidative C–C coupling to form the σ -alkyl- π -allyl intermediate; 2) protonation cocatalyzed by the protic solvent to yield a cationic allyl-alkene species; 3) nucleophilic attack of the amine with concomitant reduction to Pd(0); and 4) proton abstraction to give the final product. Depending on the pK_a of the solvent, the selectivity-determining step is the protonation (telomers 1, 2 are preferably formed) or the C–C coupling (telomers 3, 4 are preferred) resulting in two kinetic scenarios with different regioselectivity of telomers.

Thus, telomers head-to-head (2) and tail-to-tail (3) were obtained essentially by controlling the pK_a of the solvent, having the ligand little influence, and the best results were obtained with dppp (L2) as ligand in both cases (Scheme 2B). Changing the solvent pK_a from 11 to 19, the selectivity determining step moves from C–C coupling to protonation, and in consequence selectivity changes from telomer 2 to telomer 3. Telomer tail-to-head (1) was essentially obtained under ligand control

using L1 (Scheme 2B). However, telomer head-to-tail (4) was still elusive and obtained in low selectivities (Scheme 2B). It is worth mentioning that compound 4 presents a skeleton structure identical to natural terpenes and is a double-bond isomer of diethylgeranylamine, an intermediate in the Takasago synthesis of L-menthol.^[12]

The best reported selectivity for telomer 4 using HNEt_2 as nucleophile reached 40.6% (conversion 100%, 40 h) using $[\text{Pd}(\text{C}_3\text{H}_5)(\text{COD})]\text{BF}_4/\text{P}(\text{OMe})_3$ as catalytic system and toluene as solvent^[9] (Scheme 2A). Using MeOH as solvent, NaOMe as nucleophile, selectivity in the tail-to-head (1) reached 95% (yield 98%) using an indomuscone-based sterically encumbered phosphine,^[13] while the best selectivity in telomer head-to-tail (4) was obtained with a supported Pd/ PPh_3 catalyst and achieved 49.3% (conversion 10.6%, 70 °C, 7 h).^[14] These results confirm our previous observation that telomer tail-to-head (1) is selectively obtained in protic medium under ligand control, and that



Scheme 3. DFT-based proposed mechanism for isoprene telomerization.^[11]

good selectivities in the head-to-tail telomer (**4**) are still elusive. In this work, we expanded the screening of ligands, including phosphites and phosphoramidites, focusing on telomer **4** formation in competition with telomer **3** to find the optimal catalytic conditions for regioselective synthesis of these telomers (Scheme 2C).

2. Results and Discussion

In Scheme 2B, it can be observed that using aprotic or high pK_a protic solvents such as ⁱPrOH, telomers **3** and **4** were preferably obtained. Telomer **4** was obtained in medium–low selectivity along with significant amounts of telomer **3**. Since the protonation step requires a protic cocatalyst in the catalytic cycle (Scheme 3), aprotic solvents must not be anhydrous, otherwise the reaction does not proceed as we have shown in a previous contribution.^[11] In acidic protic solvents, the ligand was able to shift the regioselectivity from telomer **2** to **1**, and therefore, it is reasonable to think that selectivity in telomer **4**, similarly to telomer **1**, will also be under ligand control in aprotic solvents.^[11] In this context, and after the study already performed with phosphines,^[11] we undertook a systematic study of ligands (phosphites and phosphoramidites). In addition, the reaction conditions were also investigated, mainly in non-protic solvents and controlling the amount of water to assess the limits of the selectivity toward telomers **4** and **3** obtained under these conditions.

2.1. Telomerization of Isoprene Using Phosphite Ligands

The catalytic system [Pd(C₃H₅)(COD)]BF₄/phosphites had provided the best selectivities in telomer **4** (Scheme 2A). In this context we undertook a systematic study aiming at exploring the influence of cone angle of phosphite ligands in isoprene telomerization. Ligands **L3–L7** with cone angle^[15] between 101°–

175° were selected. [Pd(C₃H₅)(COD)]BF₄ was chosen as catalysts precursor working initially in nonanhydrous THF as non-protic solvent, and in conditions similar to the previously studied with phosphines to facilitate comparison of results.

When the reaction was conducted with the high cone angle phosphite **L3** (175°), high yield (81%) and high selectivity toward telomer **3** (87%) was obtained (Table 1, entry 1). An increase in temperature to 40 °C, allowed to achieve 91% yield with the selectivity on **3** practically unchanged (Table 1, entry 2). The use of **L4** provided excellent yield (94%) but a poor selectivity (entry 3). Selectivity to **4** was boosted up to 44% (46% for **3**) when **L5** was used, but yield dropped to 16% (entry 4). The use of phosphites with even smaller cone angle such as **L6** and **L7**,^[16] (107° and 101°, respectively) provided high yields (91% and 80%, respectively) and relatively high selectivities in telomer **4** (40% and 43%, respectively) (entries 6 and 8). In both cases, telomer **3** was obtained in similar selectivity as telomer **4**. These results suggest a tendency that smaller phosphites favor the formation of telomers **3** and **4** in about the same proportion, while the bulky phosphite (**L3**) clearly favors the formation of **3**. Similar results of selectivity with ligands **L5** and **L6** were previously reported performing the reaction in THF and toluene, respectively, for 40 h (Table 1, entries 5 and 7).^[9] Notice that in our case, the reaction was performed for 24 h for the sake of comparison with the previous work with phosphines. The systematic variation on the phosphite cone angle intended to clarify the influence of the ligand bulkiness on selectivity; but while the bulky ligand **L3** allowed to obtain telomer **3** selectively, smaller cone angle phosphites (**L4–L7**) seems to exert a less significant influence. According to our previous, detailed mechanistic study on the regioselectivity control of this reaction, the selectivity for telomers **3** and **4**, can be largely determined by the protonation step (see Scheme 3), which can be influenced by other properties of ligands, different than bulkiness. Due to these multiple factors, no clear correlation of the selectivity with the cone angles could be drawn.^[11]

Then, we undertook a study of the reaction conditions using ligands **L3** and **L7** to improve selectivity in telomers **3** and **4**, respectively. The increase in the Pd loading up to 1 and 3 mol% with the catalytic system Pd/**L3**, produced a decrease of the selectivity on telomer **3**, and slightly increased the formation of telomers **1** and **4** (Table S1). The addition of NEt₃ (15 mmol), that had previously allowed to increase the selectivity toward telomer **3**, produced a similar effect but afforded a drastic reduction in yield (22%).

Taken into account these data, we decided to perform the reaction at 40 °C and to test other aprotic solvents to assess their influence in the selective obtention of telomer **3** (Figure 1). In solvents, such as THF, DMF, hexane, toluene, and ethyl ether, telomer **3** was always obtained in high selectivity (up to 94% in hexane and toluene) but notable changes in yield were observed. DCM provided a different behavior since yield was good but the selectivity on **3** was very low. The best combination yield/selectivity was found using Et₂O giving a 90% yield and 90% selectivity toward **3**.

These results are similar to those obtained with the Pd(OAc)₂/PPh₃/DMF/NEt₃ system,^[11] and slightly lower than

Table 1. Pd-catalyzed telomerization of isoprene using phosphites L3-L7 with HNEt₂.^{a)}

Entry	Ligand	Yield (%)	Ratio 1/2/3/4
1	L3	81	6/0/87/7
2 ^{b)}	L3	91	7/0/85/8
3	L4	94	39/7/25/29
4	L5	16	10/0/46/44
5 ^{c), d)}	L5	16	15.4/4.1/45.4/35
6	L6	91	22/3/35/40
7 ^{c), d), e)}	L6	100	27.8/2.4/31.3/38.5
8	L7	80	12/2/43/43
9 ^{f)}	L7	23	2/0/50/48

Ligand:	L3	L4	L5	L6	L7
Cone angle (°):	175	130	128	107	101

^{a)} Conditions: [Pd(C₃H₅)(COD)]BF₄ (0.05 mmol); L (0.075 mmol); isoprene (10 mmol); NHEt₂ (9.6 mmol); THF (2 mL, water content < 200 ppm); 24 h; room temperature.
^{b)} 40 °C.
^{c)} Ref. [9].
^{d)} Conditions: [Pd(C₃H₅)(COD)]BF₄ (0.012 mmol); L (0.012 mmol); isoprene (2.5 mmol); NHEt₂ (2.4 mmol); THF (0.25 mL); 40 h; room temperature.
^{e)} In toluene. Yield 100 %, selectivity: 19.5/21.3/18.6/40.6.
^{f)} HNIPr₂, ratio isoprene/ HNIPr₂ = 0.48.

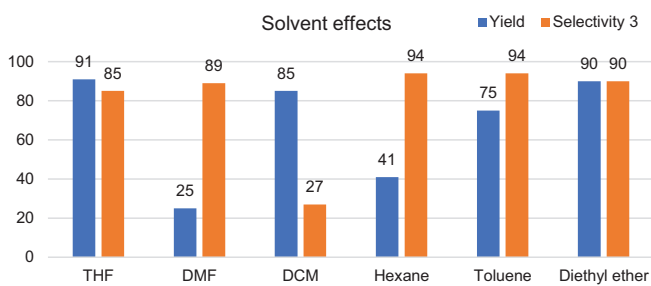


Figure 1. Influence of solvents in the selectivity of isoprene telomerization affording telomer 3 with the [Pd(C₃H₅)(COD)]BF₄/L3 catalytic system. Conditions: [Pd(C₃H₅)(COD)]BF₄ (0.05 mmol); L3 (0.075 mmol); isoprene (10 mmol); NHEt₂ (9.6 mmol); solvent (2 mL); 24 h; room temperature. All the reactions were performed in a sealed flask.

when using dppp, with the advantage of using lower temperatures and no additives.

A similar study on the reaction conditions using [Pd]/L7 as catalytic system allowed to discover that, among different precursors tested, only [Pd(C₃H₅)(COD)]BF₄ provided telomerization products (Table S2). The other tested palladium precursors (PdCl₂, Pd(OAc)₂, and Pd₂(dba)₃) did not provide telomerization products.

The Pd loading had little effect in activity or selectivity in the range 0.5–3 mol% since yields (75%–82%) and selectivity to 4 (43%–35%) were of the same order (Table S3). The Pd/L ratio in the range 1:0.5–1:1.5 also afforded similar results. However, a

large excess of ligand (4 equiv.) in the reaction medium blocked the catalytic system and, consequently, no telomerization products were formed (Table S4). In the absence of ligand, the yield was very low (6%) and selectivity shifted to telomer 1. The reaction temperature had a clear effect on activity (Table S5). When the reaction was carried out at 80 °C, yield (92%) increased with respect to that obtained at room temperature, although selectivity toward telomer 4 (38%) slightly decreased in a proportion similar to the increase in 3.

A study of different solvents showed that THF, diethyl ether, DME, and toluene provided the best results of yield and selectivity toward 4 (Figure 2). In the other solvents, the selectivity for telomer 4 was below 20%.

The selectivity of the reaction over time was also evaluated under the [Pd(C₃H₅)(COD)]BF₄/L7/THF system using HNEt₂ as nucleophile at 10 g scale and no significant variation on selectivity along the time was observed (Figure S1). This also indicates that the products are not interconverted (isomerization) along the reaction time.

Finally, different nucleophiles were tested observing that more bulky amines afforded lower yields, although the selectivity in telomer 4 reached 48% using HNⁱPr₂ in 23% yield (Table 1, entry 9; Table S6). This is the best selectivity reported for 4 using an amine as nucleophile. Telomer 3 was obtained in similar amounts (50%), together with only 2% of telomer 1. Different isoprene/amine ratios or the slow addition of the amine had no influence in the selectivity.

Table 2. Pd-catalyzed telomerization of isoprene using phosphoramidites L8–L12 with HNEt₂.^{a)}

Entry	Ligand	Yield (%)	Ratio 1/2/3/4
1	L8	53	18/3/47/32
2	L9	82	38/5/29/28
3	L10	93	13/2/46/39
4	L11	93	41/8/29/22
5	L12	67	27/4/33/36

^{a)} Conditions: [Pd(C₃H₅)COD]BF₄ (0.05 mmol); L (0.075 mmol); isoprene (10 mmol); HNEt₂ (9.6 mmol); THF (2 mL, water < 200 ppm); 24 h; room temperature.

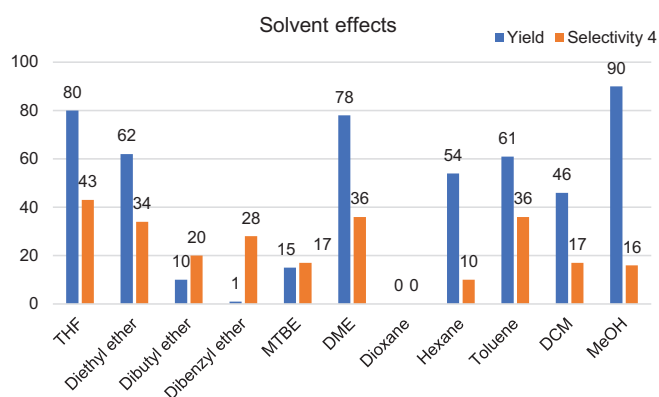


Figure 2. Influence of solvents in the selectivity of isoprene telomerization affording telomer 4 with the [Pd(C₃H₅)(COD)]BF₄/L7 catalytic system. Conditions: [Pd(C₃H₅)(COD)]BF₄ (0.05 mmol); L (0.075 mmol); isoprene (10 mmol); HNEt₂ (9.6 mmol); solvent (2 mL); 24 h; room temperature.

2.2. Telomerization of Isoprene Using Phosphoramidite Ligands

Phosphoramidites are an attractive monodentate class of ligands for their facile synthesis as well as high stability.^[17] Indeed, modifications in either the amine or in the diol moiety allows to tune the steric hindrance of the ligand and therefore a change on selectivity should be expected.^[18] To the best of our knowledge, these ligands have never been tested in telomerization. Ligands L8–L12^[19] bearing different modifications in the amine moiety and bis-naphthol or bis-phenol backbone were selected to determine their influence on the selectivity of telomer 3 versus 4.

The catalytic systems [Pd(C₃H₅)(COD)]BF₄/L8–L12 were tested in THF and HNEt₂ as nucleophile in conditions similar to the previous study with phosphite ligands. The most relevant results are summarized in Table 2. A mixture of the four linear telomers was obtained with all ligands. Telomers 3 and 4 were obtained in preference to telomers 1 and 2, as expected when working

in aprotic solvents. Yields were in general high and selectivities low, and the best result was obtained with ligand L10 (Table 2, entry 3) providing 93% yield and a selectivity of 46% and 39% for telomer 3 and 4, respectively. Ligands L8 and L12 also provided selectivities higher than 30% in telomers 3 and 4, but yields were lower (Table 2, entries 1 and 5). Ligand L11 that afforded high yield provided a low selectivity in telomers 3 and 4.

The phosphoramidites tested in isoprene telomerization afforded high yield. However, selectivity for both telomers 3 and 4 were always lower than those obtained with phosphite ligands.

2.3. Study of the Influence of the Amount of Water in THF

As discussed in the introduction, DFT calculation and microkinetic simulations performed with the catalytic system [Pd(C₃H₅)(COD)]BF₄/PPh₃ and Et₂NH as nucleophile, indicate that the pK_a of the protic solvents control the selectivity, while in aprotic solvents the amount of water impurities governs the isomer distribution. For protic solvents, low pK_a values (acidic) and large amount of water favour the formation of telomers 1 and 2, with the prevalence of telomer 2 for most ligands. At high pK_a values and low water amount, the formation of telomers 3 and 4 is favoured, but the former predominates. The percentage of isomer 4 is optimal at intermediate pK_a values for the solvent (around pK_a = 19, e.g. 2-propanol), although simulations predict that the percentage of 4 would be always below 60%. This catalytic system afforded 36% and 37% of telomer 4 when the reaction was performed in propanol or 2-propanol, respectively (see Table 4, entries 1 and 2).^[11]

In aprotic solvents, it has been observed^[11] that residual amounts of water change the selectivity of the system. To quantify this effect, we performed a study with the catalytic system [Pd(C₃H₅)(COD)]BF₄/PPh₃ and Et₂NH as nucleophile, starting with anhydrous THF, adding controlled amounts of water ranging from 0.2 to 4.0 mmol. The results are presented in Table 3.

Table 3. Effect of water concentration in THF on telomer selectivity.^{a)}

Entry	Water (mmol)	Ratio 1/2/3/4
1	–	27/7/33/33
2	0.2	23/4/36/37
3	0.4	17/4/42/37
4	1	18/4/39/39
5	2.0	15/4/44/37
6	4.0	20/3/37/40

^{a)} Conditions: [Pd(C₃H₅)(COD)]BF₄ (0.05 mmol), PPh₃ (0.075 mmol), isoprene (10 mmol), HNEt₂ (10 mmol), THF (2 mL, water < 20 ppm), 24 h, 35 °C.

The general tendency observed with the increase in amount of water, in the range studied, was the initial slight decrease in selectivity for telomer 1 and 2 and the small increase in selectivity for telomers 3 and 4, which were formed in comparable amounts. When 4 mmol were added, the tendency started to reverse, and the ratio of telomers 3/4 was practically maintained, which shows the difficulties to modify the ratio of these telomers.

2.4. Screening for Sustainable Solvents

Solvents play a pivotal role in the sustainability of chemical processes. For example, in pharmaceutical industry, it is estimated that solvents account for 70% of all mass and 60% of the energy consumption.^[20] Therefore, the search for greener and more sustainable solvents is of utmost interest for the overall sustainability of a process. Solvent guides assessing their health risks, environmental impact, safety of use, and disposal have been developed.^[21] In this vein, we tested a set of solvents regarded as green, sustainable or renewable in the telomerization of isoprene with diethylamine (Table 4). 1-propanol and 2-propanol, which have an optimal pK_a to obtain telomer 4,^[11] are also solvents with good sustainability parameters,^[21] and the results with the catalytic system [Pd(C₃H₅)(COD)]BF₄/PPh₃ as catalytic system are presented in Table 4 (entries 1 and 2).^[11] Using the same catalytic system, propylene carbonate was tested first as solvent (entry 3), and a biphasic system was formed after the reaction, but unfortunately the products were distributed in both phases.

Using the high boiling points 1,3-dimethyl-2-imidazolidinone (DMI, entry 4), cyrene (entry 5), and triacetin (triacetoxypropane, entry 6), the products could not be isolated by solvent evaporation using our standard protocol and only the selectivity was determined. Furthermore, different products, assumed as double bond isomerization telomers were formed, corresponding to 2%–4% in the telomer distribution. These isomers were also observed in anisole as solvent (3%, entry 7). In all cases selectivity was low, and telomers 1, 3, and 4 in different proportions were mainly obtained. Considering that ether solvents provided the best result for telomers 3 and 4 (Figures 1 and 2), we decided

to test more sustainable ether solvents. Using cyclopentylmethyl ether (CPME, entry 8) and the biorenewable 2-MeTHF (entry 9), a similar mixture was obtained, and results were comparable to 1-propanol. The addition of 2.0 mol L⁻¹ of water to 2-MeTHF resulted in a decrease of telomers 1 and 2 and an improved selectivity for telomers 3 and 4, that were formed in comparable amount. Thus, CPME and 2-MeTHF appear as suitable non-protic alternative solvents for performing telomerization of isoprene.

3. Conclusion

In this work we have carried out a systematic study of palladium-catalyzed isoprene telomerization using diethyl amine as nucleophile, with the aim of exploring the limits of the selectivity in aprotic conditions toward telomers 3 and 4. To this purpose, we have studied the use of phosphites with different cone angles, as well as phosphoramidites, as ligands, employing [Pd(C₃H₅)(COD)]BF₄ as catalyst precursor in THF. Concerning the use of phosphite ligands, excellent results in telomer 3 were obtained using the bulky phosphite L3, cone angle 175° and THF (91% yield and 85% selectivity) or ethyl ether (90% yield and 90% selectivity), not requiring the use of additives. However, better selectivity in telomer 4 was achieved with phosphites with small cone angle, L6 (107°) and L7 (101°), the latter providing the best selectivities for telomer 4 reported to date using amines as nucleophiles (48% with HNⁱPr₂). The study of the effect of progressively increasing the amount of water starting from an anhydrous THF, using [Pd(C₃H₅)(COD)]BF₄/PPh₃, afforded selectivities around 40% for telomers 3 and 4, similar to those obtained in propanol or 2-propanol, but there is a limit in this improvement. In a screening for more sustainable solvents, CPME and particularly 2-MeTHF, a solvent obtained from lignocellulosic biomass, stood out as good alternatives to replace THF.

4. Experimental Section

General procedure for telomerization with amines: palladium precursor ([Pd(C₃H₅)(COD)]BF₄, 0.05 mmol), phosphine (0.075 mmol), isoprene (1 mL, 10 mmol), diethylamine (1 mL, 9.6 mmol), and sol-

Table 4. Sustainable solvents for isoprene telomerization with diethylamine.^{a)}

Entry	Solvent	Yield (%)	Ratio 1/2/3/4
1 ^{b)}	1-Propanol	46	24/4/36/36
2 ^{b)}	2-Propanol	38	13/3/47/37
3 ^{c)}	Propylene carbonate	n.d.	38/26/14/22
4	DMI	n.d.	33/7/25/34 ^{d)}
5	Cyrene	n.d.	36/28/12/20 ^{d)}
6	Triacetin	n.d.	31/7/25/35 ^{d)}
7	Anisole	72	39/9/24/25 ^{d)}
8	CPME	84	20/7/35/37
9	2-MeTHF	86	26/4/32/38
10 ^{e)}	2-MeTHF	52	9/5/43/42 ^{d)}

^{a)} Conditions: [Pd(C₃H₅)(COD)]BF₄ (0.05 mmol), PPh₃ (0.075 mmol), isoprene (10 mmol), HNEt₂ (10 mmol), solvent (2 mL, water < 200 ppm), 24 h, 35 °C.
^{b)}].Ref. [11]
^{c)} Two phases were observed after reaction.
^{d)} The difference to 100% correspond to double-bond isomers.
^{e)} Water (4.0 mmol) was added.
 DMI: 1,3-dimethyl-2-imidazolidinone (water < 0.2%); CPME: cyclopentylmethyl ether; Triacetin: triacetoxyp propane (water < 0.2%).

vent (2 mL) were stirred in a sealed flask at the corresponding temperature. The volatiles were removed in a rotary evaporator and the residue was distilled under vacuum. The resulting oil was weighed and the yield determined. The selectivity was determined by GC–MS.

Supporting Information

Synthetic procedures including ligands and catalysts synthesis, catalytic procedures, tables of variables optimization, and GC–MS characterization.

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Conflict of Interests

The authors declare no conflicts of interest.

Data Availability Statement

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

Keywords: Isoprene · Ligand control · Palladium · Solvent control · Telomerization

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