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# Palladium-Based Telomerization of 1,3-Butadiene with Glycerol Using Methoxy-Functionalized Triphenylphosphine Ligands

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*Dedicated to Professor Jan Reedijk on the occasion of his 65th birthday and his retirement*

**Abstract:** Glycerol is considered a potential renewable building block for the synthesis of existing as well as new chemicals. A promising route is the telomerization of 1,3-butadiene with glycerol leading to $C_8$ chain ethers of glycerol with applications in, for example, surfactant chemistry. Recently, we reported a new set of palladium-based homogeneous catalytic systems for the telomerization of 1,3-butadiene with glycerol and found that palladium complexes bearing methoxy-functionalized triphenylphosphine ligands are highly active catalysts capable of converting crude glycerol without any significant loss of activity. Herein, we present a detailed account of these investigations by reporting on the influence of the butadiene/glycerol ratio, temperature, and reaction time on product selectivity and activity allowing further optimization of catalyst performance. Maximum activity and yield were reached for high 1,3-butadiene/glycerol ratios at a temperature of 90 °C, whereas the selectivity for mono- and diethers of glycerol could be optimized by combining high reaction temperatures and short reaction times with low butadiene/glycerol ratios. Variation of the $Pd^{II}$ metal precursors and the metal/ligand ratio showed that palladium precursors with halogen ligands gave unsatisfying results, in contrast to precursors with weakly coordinated ligands such as $[Pd(OAc)_2]$ and $[Pd(acac)_2]$. $[Pd(dba)_2]$, the only $Pd^0$ precursor tested, gave the best results in terms of activity, which illustrates the importance of the ability to form a $Pd^0$ species in the catalytic cycle. Finally, base addition resulted in a shortening of the reaction time and most likely facilitates the formation of a $Pd^0$ species. Based on these results, we were able to realize the first attempts towards a rational ligand design aimed at a high selectivity for mono- and diether formation.

**Keywords:** glycerol · homogeneous catalysis · palladium · phosphines · telomerization

## Introduction

Telomerization describes the oligomerization of, for example, a conjugated diene like 1,3-butadiene in which the chain length is controlled by chain transfer (in the case of 1,3-butadiene the reaction with a nucleophile). The first telomerization was described by Smutny et al. in 1967[1] who investigated the oligomerization and dimerization of butadiene and its telomerization with phenol. Since then numerous investigations have concentrated on monofunctional nucleophiles such as ammonia[2,3] or alcohols.[4–7] Recent concerns regarding sustainable chemistry have promoted studies of sugar-based components, for example, starch,[8] sucrose,[9,10] arabinose,[11] xylose,[11] and aldose,[12,13] as nucleophiles in the telomerization of 1,3-butadiene. Regulation in the European Union is enforcing a growth in the production of biodiesel as a fuel additive or alternative, which is resulting in a

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steady increase in glycerol production as the main byproduct of biodiesel manufacturing (226 kg tonne$^{-1}$). On the other hand, more recently, there have been some concerns about the sustainability of current biodiesel production routes and last year the price of glycerol stabilized or even slightly increased. Nevertheless, alternative technologies for the conversion of crude glycerol directly into value-added products are still highly attractive. The relevance of this topic is reflected by various studies[14–17] and recent reviews[18–20] on glycerol usage that have focused, for instance, on synthesis gas production followed by Fischer–Tropsch synthesis.[20]

Johnson and Taconi[21] summarized in a recent review the possibilities and economic considerations concerning the utilization of crude glycerol. The authors concluded that technologies for the direct conversion of crude glycerol have the potential to facilitate the entrance of glycerol as an important feedstock into the chemical market. Nevertheless, potential processes require the transformation of cheap starting materials into value-added products with reasonable market size.

In this regard, we have started to investigate the use of glycerol as an attractive nucleophile in the telomerization of 1,3-butadiene leading to $C_8$ chain ethers of glycerol with potential applications in surfactant chemistry or as chemical building blocks. Surprisingly, just one publication concerning the telomerization of butadiene with glycerol and other glycols exists in the open literature.[22] Therein, Behr and Urschey used a Pd/TPPTS (TPPTS = triphenylphosphine tri-*m*-sulfonate trisodium salt) complex as a catalyst for this reaction, which reached a turnover frequency (TOF) of 248 h$^{-1}$ with turnover numbers (TONs) of around 990 with a total TON of 3300 as the catalyst could be recycled five times. Concerning the use of crude glycerol as a substrate in the telomerization process, to the best of our knowledge, no investigations have yet been performed, at least none have been reported in the open literature. The limited knowledge of glycerol as a nucleophile together with the challenge of realizing the direct telomerization of crude glycerol inspired us to investigate potential catalyst systems for this reaction type. Points of major importance for the industrial feasibility of this reaction include improved catalyst activity, control of selectivity, product separation, and potential possibilities for catalyst recycling. The main focus of our investigations concerned catalyst activity and selectivity. Nevertheless, the simplicity of product separation may be mentioned because phase separation between the polar glycerol layer and the less or non-polar glycerol ethers occurs and significantly facilitates not only product separation but also glycerol re-cycling.

In a recent communication[23] we briefly reported on palladium-based complexes with methoxy-functionalized triphenylphosphine ligands as highly active catalysts in the telomerization of 1,3-butadiene with glycerol. The triphenylphosphine ligands were varied from one methoxy group on just one phenyl ring to up to three methoxy groups on each ring (Figure 1). A maximum catalytic activity was found for TOMPP (tris(*o*-methoxyphenyl)phosphine; ligand **C** in Figure 1), which bears one methoxy group in the *ortho* position of each ring. By using a Pd/TOMPP complex in the telomerization of glycerol, TONs of up to 1520 in one run and a TOF of 3040 h$^{-1}$ could be reached. In addition, by reducing the amount of catalyst, even higher TONs of 8545 with a TOF of 3418 h$^{-1}$ could be realized. We could identify several factors that are crucial for high catalytic activity, including increased electron density on the phosphorus atom and medium steric hindrance. Polar groups were identified as advantageous due to an improved solubility of the catalyst system in polar substrates such as glycerol. In addition, modification of the phenyl rings at the *ortho* position appeared to be essential, which illustrates the influence of the ligand cone angle[24] and points towards the formation of hemilabile species,[25] including a P–Pd–O bond that stabilizes the catalyst system, as shown for ruthenium-based complexes.

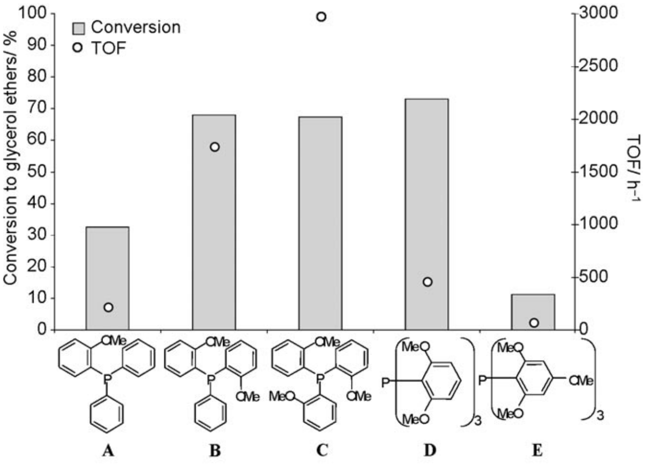
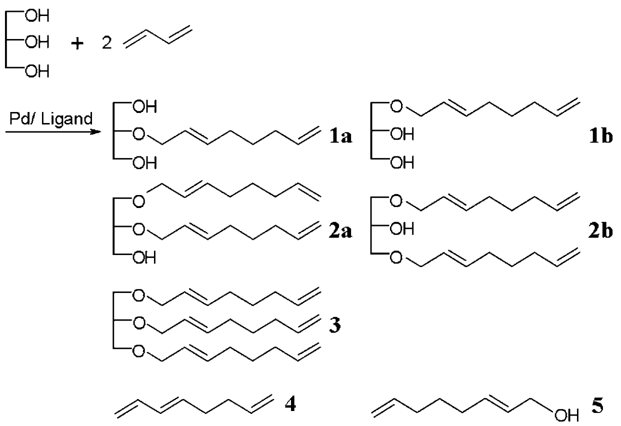


Figure 1. Catalytic activity of different methoxy-functionalized ligands in the telomerization of 1,3-butadiene with glycerol (0.06 mol % [Pd(acac)$_2$] based on glycerol, butadiene/glycerol = 2.5, reaction time = 5 h or until the pressure dropped to 1 bar, $T$ = 80 °C).

Herein we present a full account of these studies and further elucidate crucial factors for high activity and selectivity in the telomerization of butadiene with glycerol as a multifunctional nucleophile. Accordingly, we followed the reaction mechanism proposed earlier for the telomerization of butadiene with methanol[4] and could find evidence of the catalytically active species by studying the effects of different metal precursors and the ligand/metal ratio. In addition, the effects of several reaction parameters, including the butadiene/glycerol ratio, reaction temperature, reaction time, and the addition of a base, were studied to gain an insight into the experimental factors that influence the reaction kinetics and product distribution. The study was aimed not only at maximizing catalytic activity, but also at optimizing reaction conditions for the telomerization of 1,3-butadiene with glycerol by using the Pd/TOMPP system for high selectivity for the target products.

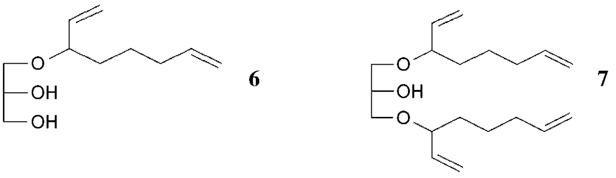
## Results and Discussion

The general reaction scheme for the telomerization of butadiene with glycerol is presented in Scheme 1. Besides the $C_8$ chain mono- (**1**), di- (**2**), and triethers (**3**) of glycerol, the butadiene dimer 1,3,7-octatriene (**4**) and, in the presence of water, 2,7-octadienol (**5**) may be formed. In addition, branched products from the telomerization of butadiene with glycerol are possible. Examples of branched mono- (**6**) and diethers (**7**) are illustrated in Scheme 2. All combinations of linear and branched $C_8$ chains are possible.

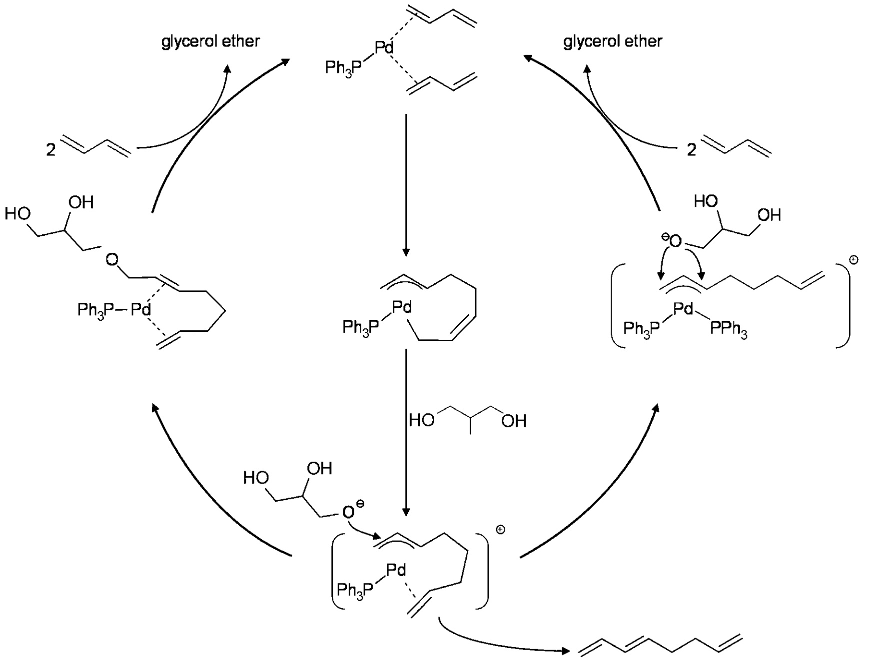


Scheme 1. Telomerization reaction of 1,3-butadiene with glycerol that results in $C_8$ chain ethers of glycerol **1**–**3** and the by-products 1,3,7-octatriene (**4**) and 2,7-octadienol (**5**).

**Proposed reaction mechanism for butadiene telomerization and the effect of experimental parameters**: Two distinct reaction mechanisms for the telomerization reactions with palladium-based complexes have been repeatedly discussed in the literature to date. Jolly et al.[26] concluded that palladium species are coordinated to one ligand during the catalytic cycle, whereas the model of Beller and co-workers[4,27] describes a catalytic species that involves an additional ligand molecule. Following the proposal of Beller et al.[4] for the telomerization of 1,3-butadiene with methanol, two molecules of 1,3-butadiene couple in the presence of palladium(0) species to form a complex that is protonated by the nucleophile, for example, methanol. In the following step the methoxide ion can add either to the C1 or C3 position of the protonated species to afford either the linear or branched product. Attack at the C1 position is sterically less hindered than attack at the C3 position. Owing to the resulting internal double bond, the linear product is thermodynamically more stable, whereas attack at the C3 position, which leads to the branched product, is electronically favored.[27] In this reaction mechanism, the formation of 1,3,7-octatriene through a side-reaction is explained by β elimination of hydrogen from the C4 position of the protonated species. In Scheme 3 we present the catalytic cycle adapted for glycerol as substrate and inspired by the work of Beller and co-workers.[4,27] For simplicity, the reaction of only one of the primary alcohol groups of glycerol is presented. The formation of di- and triethers of glycerol would require the mono- and diethers, respectively, to enter into the catalytic cycle again. Mono- and diethers that enter into the catalytic cycle exhibit enhanced steric hindrance. Thus the formation of di- and triethers of glycerol is very demanding of the catalyst system and requires a high acceptance of a sterically demanding substrate. As described above, the electronically favored attack of the nucleophile



Scheme 2. Mono- (**6**) and diether (**7**) of glycerol as examples of branched reaction products of the telomerization of 1,3-butadiene with glycerol.



Scheme 3. Proposed reaction mechanism for the telomerization of 1,3-butadiene with glycerol following the mechanism proposed by Beller and co-workers.[4,27]

at the C3 position would result in branched telomerization products. In the case of the use of glycerol as nucleophile instead of methanol, the enhanced steric hindrance of an attack at the C3 position becomes even more pronounced as glycerol is a much bulkier nucleophile than methanol. Glycerol ethers with branched chains, however, have not been observed in significant amounts in any product mixture in our study. Therefore, the greater steric hindrance experienced by the attack at the C3 position appears to outweigh the electronically favored attack.

Focussing on the linear glycerol ethers, monoether **1a** and diether **2a** are possible reaction products, but rather unlikely due to the reduced reactivity of the secondary alcohol, which is a result of an increased steric hindrance induced by the two primary alcohols and the more demanding deprotonation of secondary alcohols. In line with this, neither **1a** nor **2a** were observed in the reaction mixtures. The triether **3**, however, was formed in higher concentrations. In summary, neither branched glycerol ethers nor monoether **1a** or diether **2a** bearing an ether chain on the secondary alcohol were found in any significant amount in the product mixtures. Consequently, statements concerning a mono- or diether in the product mixture refer to the telomerization products **1b** and **2b**, respectively.

Interestingly, very few investigations on multifunctional nucleophiles exist and these mainly focus on sugar components[9–13] or starch.[8] These studies predominately report monoethers as the products independent of the butadiene/nucleophile ratio used. Indeed, higher substitutions of multifunctional nucleophiles seem to be difficult to realize. On the one hand, catalyst systems with a high acceptance for sterically demanding substrates are required. On the other, higher substituted products are less polar, which results in the formation of a two-phase system. Consequently, the formation of higher substituted products strongly depends on the solubility of the catalyst system in both the starting material and product phase, whereas the high solubility of the ligand or catalyst system in the polar layer only results predominantly in the formation of monosubstituted products, as shown by Behr and Urschey[22] who reported on the telomerization of glycerol using Pd/TPPTS, a water-soluble catalyst system, in a biphasic reaction system in which only monoethers were formed with diether formation remaining below 5%. Therefore, the high selectivity for monosubstituted telomers seems to be due to the low solubility of higher substituted ethers in the water phase that contains the catalyst.

The Pd/TOMPP catalyst system exhibits a high acceptance of sterically demanding substrates and—due to its high solubility in the product phase—even allows the formation of significant amounts of triethers.

To further elucidate the reaction progress and draw conclusions about the catalytically active species, we have investigated in more detail the effects of the metal precursor, base addition, the butadiene/glycerol ratio, as well as the ligand/metal ratio. These aspects will now be discussed. However, as stated before, several catalytic investigations concerning the telomerization of 1,3-butadiene with methanol[4–7] or ammonia[2,3] exist and report mass transport limitation at lower stirring rates. To avoid any mass transport limitations a stirring rate of 1200 rpm was chosen in all the experiments discussed.

*Effect of the metal precursor*: In a first step, the influence of the metal precursor on the reaction was investigated. Different types of metal precursors were tested, including the usually employed palladium(II) acetylacetonate ([Pd(acac)$_2$]) or palladium(II) acetate ([Pd(OAc)$_2$]), bis(dibenzylideneacetone)palladium(0) ([Pd(dba)$_2$]), palladium(II) chloride (PdCl$_2$), and palladium(II) cyclooctadiene dichloride ([Pd(cod)Cl$_2$]). The results obtained with the different palladium precursors tested under identical reaction conditions are summarized in Figure 2. We observed that metal precursors containing chloride ligands result in a very low catalytic activity of the Pd/TOMPP system in the telomerization reaction of 1,3-butadiene with glycerol. This effect may be caused by chloride ligands of the precursor binding strongly to the metal center resulting in a hindered release of the ligand and consequently hindered reduction of Pd$^{II}$ to the Pd$^0$ species required in the catalytic cycle. The other Pd$^{II}$ precursors, [Pd(acac)$_2$] and [Pd(OAc)$_2$], exhibit weakly coordinated ligands and thus reduction to Pd$^0$ should be facilitated. Accordingly, for these two palladium precursors a comparable high catalytic activity was observed. In [Pd(dba)$_2$], palladium is already present as the Pd$^0$ species. Therefore, no reduction step is needed, which results in even higher catalytic activity, most probably due to the improved availability of the metal. In summary, the correlation between the observed catalytic activity and the metal precursor used is well in line with a Pd$^0$ species being the catalytic active species in the reaction cycle, as proposed earlier.

Recent discussions on several reactions catalyzed by homogeneous complexes focused on the ability of palladium colloids to catalyze reactions. [Pd(dba)$_2$] is known to easily form colloidal solutions. We therefore performed a series of control experiments to investigate the activity of palladium colloids in the telomerization of glycerol. In a first step, [Pd(dba)$_2$] was utilized without addition of a further ligand. The reaction resulted in palladium black formation; no catalytic

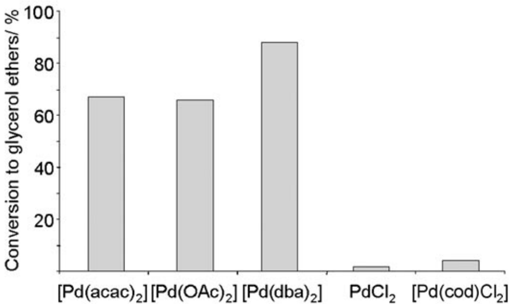


Figure 2. Variation of the metal precursor in the telomerization of 1,3-butadiene with glycerol using Pd/TOMPP complexes (0.06 mol% palladium based on glycerol, butadiene/glycerol = 2.5, P/Pd = 5, reaction time = 30 min, $T = 80\,^{\circ}C$).

activity could be observed. In addition, we also performed the commonly used poisoning experiments with mercury and poly(vinylpyridine) (PVPy). When a large excess of mercury was used in the poisoning experiment, no reaction inhibition was observed and similar TON and TOF values were reached. This strongly suggests the absence of catalytically active colloid particles in the reaction mixture. The use of excess PVPy (300 and 500 equiv) in the reaction resulted in an increase in the reaction time (and hence a lowering of the TOF), but no decrease in TON. This observation can be explained by the coordination/decoordination of PdL or $PdL_2$ species to PVPy, which is known for other catalytic systems, and causes the decrease in the observed activity. These important observations reinforce the occurrence of a truly homogeneously catalyzed reaction and the presence of PdL or $PdL_2$ as the active species.

*Effect of base addition*: Several investigations on telomerization reactions with different substrates report the positive effects achieved by the addition of a base.[10,11,28,29] Pennequin et al.[10] reported significantly increased catalytic activity after the addition of sodium hydroxide to the telomerization reaction of 1,3-butadiene with sucrose using a Pd/TPPTS catalyst system, the required reaction time for completion reducing from 2.5 h to only 26 min. Estrine et al.[11] compared the effects of several tertiary amines, including $i\mathrm{Pr}_2\mathrm{EtN}$, $Et_3N$, $i\mathrm{Pr}_2\mathrm{MeN}$, $n\mathrm{Pr}_3\mathrm{N}$, DABCO, and $i\mathrm{Pr}_3\mathrm{N}$, on the catalytic activity in the telomerization of 1,3-butadiene with L-arabinose and D-xylose. They identified $i\mathrm{Pr}_2\mathrm{EtN}$ and $Et_3N$ as the most efficient bases to improve the catalytic activity. A correlation between the strength of the base and improved activity, however, could not be observed. A commonly accepted explanation for this effect has been given by Beller and co-workers,[27] who suggested that bases predominantly facilitate the reduction of $Pd^{II}$ species to $Pd^0$ complexes, which are assumed to be the active species in the catalytic cycle, as outlined above.

Accordingly, the effect of base addition on the telomerization of 1,3-butadiene with glycerol was investigated in this work. For this purpose, $Et_3N$ was chosen as a suitable base and the effect of different butadiene/glycerol ratios was studied. The results are summarized in Figure 3 and show that comparable yields with and without base can be reached for butadiene/glycerol ratios of 1 and 2.5. The reaction times for comparable yields shorten considerably, 10 and 20 min being required for butadiene/glycerol ratios of 1 and 2.5, respectively.

Surprisingly, in the case of a butadiene/glycerol ratio of 4, a significant drop in the conversion and TOF was observed when base was added. Addition of an extra amount of base gave the same results as without base. Apparently the base/diene ratio is important, which means that other reaction pathways are kinetically relevant. Estrine et al. found in their study that a stoichiometric amount of amine and nucleophile gave the best results, but when excess amine was used a decrease in activity was observed.[11] They proposed the coordination of the base to the active species and/or interaction of the base with the nucleophile, for example, catalyzed deprotonation of the nucleophile, both of which seem plausible. In relation to our results, both facilitated reduction of $Pd^{II}$ and deprotonation of the alcohol by the base to generate the nucleophile may occur. However, the somewhat unexpected result for base addition in the case of a butadiene/glycerol ratio of 4 may be caused by the high dilution of the system and the consequently lower base/diene ratio. Nevertheless, the exact role of the base within the catalytic cycle has to be investigated further.

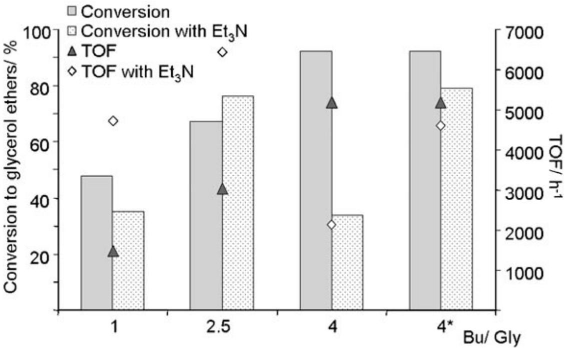


Figure 3. Effect of $Et_3N$ addition on the yield and TOF in the telomerization of 1,3-butadiene with glycerol (0.06 mol% $[Pd(acac)_2]$ based on glycerol, P/Pd = 5, glycerol/$Et_3N$ = 10, *glycerol/$Et_3N$ = 20, $T$ = 80 °C, reaction time without base = 30 min).

*Effect of the ligand/metal ratio*: To allow comparison with literature data, $[Pd(acac)_2]$ as the most common metal precursor for this reaction, was used in all further investigations. The ligand/metal ratio was varied between 1 and 10. Interestingly, the catalytic activity was found to be independent of the amount of ligand for a ligand/metal ratio of 2 or more (Figure 4). A low catalytic activity for a ligand/metal ratio of 1 results in catalyst decomposition and palladium black formation due to ligand concentrations that are too low to allow the efficient formation of the required catalytically active species. Bearing in mind the dynamic equilibrium of different $PdL_x$ species in solution, a minimum ligand concentration appears to be required to form the catalytically active species. Although the results do not allow conclusions to be drawn on whether the active species in the reac-

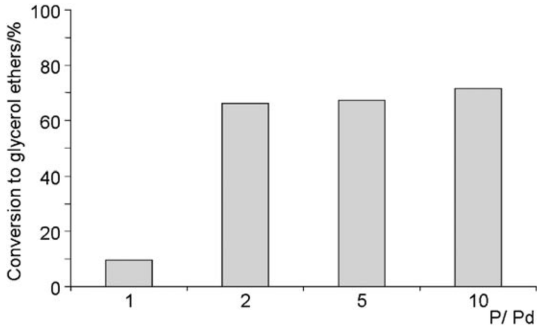
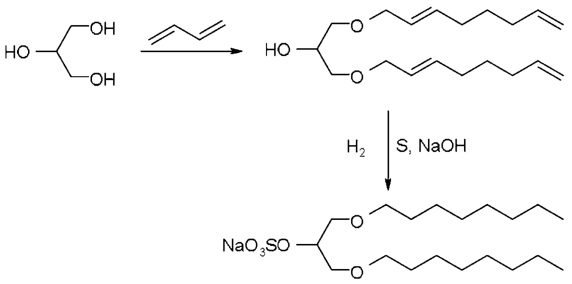


Figure 4. Effect of the TOMPP/Pd ratio on the catalytic activity in the telomerization of 1,3-butadiene with glycerol (0.06 mol% $[Pd(acac)_2]$ based on glycerol, reaction time = 30 min, $T$ = 80 °C).

tion cycle is a one or two ligand complex, the minor changes in the catalytic activity for a ligand/metal ratio of 2 or more point towards a minimum required L/Pd ratio of 2 for optimal activity.

**Telomerization of butadiene towards target molecules**: An important issue in the telomerization of butadiene with polyols such as glycerol is the selectivity for target products. In the case of glycerol, glycerol mono- and especially diethers present ideal target molecules as subsequent hydrogenation followed by sulfonation allows direct excess to potential detergent molecules (Scheme 4).

*Rational ligand design*: High selectivity for glycerol diethers as target molecules necessitates the telomerization of previously formed $C_8$ chain glycerol monoethers. Consequently, potential catalyst systems require a high acceptance of sterically demanding substrates and a certain solubility in the less polar product phase. As discussed already, the Pd/TPPTS system described by Behr and Urschey[22] shows selectivities of around 95% for the monoether of glycerol, with just small amounts of diether formed and no triether due to the low solubility of the catalyst in the less polar product layer. In addition, the system shows a somewhat low activity, with TOFs of 248 $h^{-1}$ and maximum TONs of 990 in 5 h.[22] In contrast, for the Pd/TOMPP catalyst systems, significant amounts of di- and triethers of glycerol are formed. Accordingly, this may indicate both a high acceptance of sterically demanding substrates and solubility in both phases of the reaction system, as further indicated by the formation of triethers, which points towards the ability to telomerize even sterically demanding nucleophiles such as bulky secondary alcohols.



Scheme 4. Telomerization of 1,3-butadiene with glycerol leading to a diether that is subsequently hydrogenated and sulfonated for detergent applications.[30]

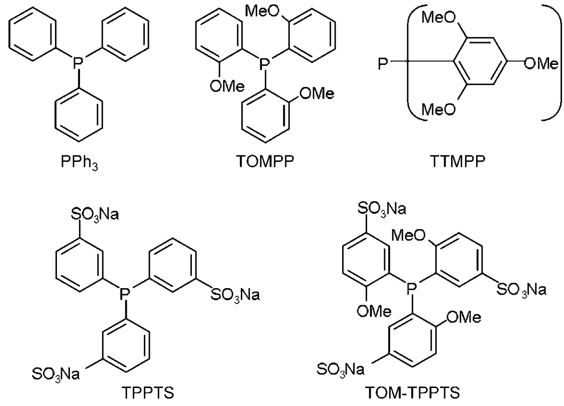
The activities and product distributions for Pd/$PPh_3$ with different ligand substitutions measured under identical reaction conditions are summarized in Table 1. Interestingly, use of the Pd/$PPh_3$ system as catalyst in the telomerization of glycerol also results in the formation of mono-, di-, and triethers of glycerol, although only TOFs of 143 $h^{-1}$ in a reaction time of 5 h could be reached (Table 1, entry 1, and Scheme 5).

Table 1. Activities and selectivities of palladium-based catalysts with different substituted $PPh_3$ ligands in the telomerization of 1,3-butadiene with glycerol.[a]

| Entry | Ligand | $t$ [h] | Selectivity[b] [%] 1 | 2 | 3 | TOF[c] [$h^{-1}$] |
|---|---|---|---|---|---|---|
| 1 | $PPh_3$ | 5 | 58 | 31 | 11 | 143 |
| 2 | TOMPP | 0.5 | 58 | 29 | 14 | 3040 |
| 3 | TPPTS | 5 | 96 | 4 | 0 | 259 |
| 4 | TOM-TPPTS[d] | 5 | 93 | 7 | 1 | 137 |
| 5 | TTMPP | 5 | 69 | 28 | 2 | 252 |

[a] Catalyst conc. = 0.06 mol% [$Pd(acac)_2$] based on glycerol, butadiene/glycerol = 2.5, P/Pd = 5, $T$ = 80 °C. [b] Based on glycerol ethers. [c] Based on glycerol conversion to glycerol ethers. [d] P/Pd = 2.5.

Based on this finding, one may conclude that the solubility of the ligand or catalyst system is the main effect influencing the product distribution rather than electronic or steric effects induced by the ligand substituents. Nevertheless, a true discrimination between pure solubility effects and the effects of ligand substituents in terms of electronic and steric effects or as directing groups is difficult to rationalize. Earlier investigations showed variations in reaction rate and product distribution to be dependent on the number of methoxy-substituents on the phenyl rings of the $PPh_3$ ligands.[23] All Pd/$PPh_3$ catalysts with methoxy-functionalized phenyl rings led to the formation of mono-, di-, and triethers of glycerol. Interestingly, however, the selectivity for mono- and diether formation increased when a high number of substituents were present on the phenyl rings, as in case of TTMPP (tris(trimethoxyphenyl)phosphine), although nearly no glycerol triether was formed. This product distribution may be attributed to the increasing polarity of the ligand with increasing number of methoxy substituents together with increasing steric constraints for the coordination of glycerol diether as substrate.



Scheme 5. Ligands with different substitution patterns on the phenyl rings, tested as palladium-based catalysts in the telomerization of 1,3-butadiene with glycerol.

Consequently, a rationalization of the dependency between ligand substitution and the resulting product distribution will be required. Based on a deeper understanding of the structure–activity relationship, the rational design of catalysts with high TOFs, as reached by the Pd/TOMPP system, and high selectivities for target molecules should be possible.

Our first attempts on a rational ligand design that combines the high activity of the Pd/TOMPP system with the high selectivity of the Pd/TPPTS system for mono- and diethers are presented below. A ligand that possesses both functional groups, methoxy groups in the *ortho* position and sulfonate groups in the *meta* position, in the phenyl rings has been reported previously.[29] With this ligand type we hoped to combine the apparent features of TOMPP that allow surprisingly high TOFs in the telomerization process with an improved solubility of the corresponding complex in the more polar glycerol phase of the reaction. The improved solubility in the glycerol layer should consequently allow us to shift the product distribution towards higher selectivities for monoether formation. The structures of the investigated functionalized $PPh_3$ ligands, including $PPh_3$ without substitution, TOMPP, TTMPP, TPPTS, and TOM-TPPTS, which bears methoxy and sulfonate groups, are illustrated in Scheme 5. As mentioned above, TOMPP and $PPh_3$ allow the formation of mono-, di-, and triethers of glycerol, whereas TPPTS exhibits a high selectivity for monoether formation.

Indeed, telomerization of glycerol using TOM-TPPTS as the ligand resulted in a product distribution comparable to the reaction with TPPTS. Unfortunately, the TOF dropped to about 137 $h^{-1}$. This disappointing result reflects the need of further mechanistic investigations. Consequently, future attempts will focus on systematic ligand modifications that will allow a deeper understanding of the structural requirements for telomerization towards certain target molecules.

Nevertheless, addressing mono- and diether formation as target molecules, we have investigated the feasibility of influencing the product distribution of the telomerization reaction with Pd/TOMPP as the catalyst system by varying several reaction parameters, including the ligand/metal ratio, the butadiene/glycerol ratio, reaction temperature, reaction time, and base addition.

*Ligand/metal ratio*: We observed that the ligand/metal ratio clearly affects the product distribution. Table 2 summarizes the product distributions and reaction rates for ligand/metal ratios between 1 and 10. As mentioned before, the overall reaction yield increases on going from a ligand/metal ratio of 1 to 2, which results in a significant increase in the TOF from 444 to 4196 $h^{-1}$. The variations in the TOF for a ligand/metal ratio between 2 and 10, however, are caused by a variation in the product distribution as the formation of triethers requires the catalytic cycle to be repeated three times. For low conversions in the case of a ligand/metal ratio of 1, 64 % selectivity for monoether formation is reached with very little triether formed. This value drops for higher ligand/metal ratios and around 20 % of the triether is formed. Interestingly, a combination of high reaction rate and little triether formation occurs for a ligand/metal ratio of 5. Prinz et al.[2] studied the telomerization of butadiene with ammonia and observed an optimum ligand/metal ratio of around 2.5 for a high reaction rate and a high selectivity for the mono-telomer, whereas higher ratios lead to enhanced dimer formation and a branched product. For the telomerization of butadiene with ethylene glycol, Behr and Urschey[22] also reported the highest activity for ligand/metal ratios between 2 and 4, whereas low (0.25) and high values (8) resulted in negligible telomer formation and catalyst decomposition. In our investigation, partial catalyst decomposition has only been observed for a ligand/metal ratio of 1 and not for higher values.

Table 2. Selectivity and reaction rate for different ratios of TOMPP/palladium in the telomerization of 1,3-butadiene with glycerol.[a]

| Entry | P/Pd | $t$ [h] | Selectivity[b] [%] 1 | 2 | 3 | TOF[c] [$h^{-1}$] |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.5 | 64 | 34 | 2 | 444 |
| 2 | 2 | 0.5 | 30 | 49 | 21 | 4196 |
| 3 | 5 | 0.5 | 58 | 29 | 14 | 2954 |
| 4 | 10 | 0.5 | 36 | 45 | 19 | 4394 |

[a] Catalyst conc. = 0.06 mol % $[Pd(acac)_2]$ based on glycerol, butadiene/glycerol = 2.5, $T$ = 80 °C. [b] Based on glycerol ethers. [c] Based on glycerol conversion to glycerol ethers.

In summary, the optimum ligand/metal range for palladium-based complexes using phosphine ligands seems to be between 2 and 4 in terms of catalyst activity, independent of the nucleophile used in the telomerization reaction. In the case of glycerol, however, an optimum in terms of maximized mono- and diether formation can be found for a ligand/metal ratio of 5, whereas both lower and higher ligand/metal ratios cause enhanced formation of di- and triethers of glycerol. The impact of the ligand/metal ratio on the product distribution could not be rationalized, although the results seem to point towards varying concentrations of PdL or $PdL_2$ as the active species depending on the concentration of ligand present in the reaction mixture.

*Effect of the butadiene/glycerol ratio*: We varied the butadiene/glycerol ratio to investigate the impact on yield, TOF, and product distribution. TOF and yield increase with an increasing butadiene/glycerol ratio, reaching a maximum for a ratio of 4 with yields up to 92 % and a TOF of 5182 $h^{-1}$ and decrease again for higher butadiene/glycerol ratios (Table 3). One reason for the reduced activity at butadiene/glycerol ratios above 4 may be a change in reactor loading. Owing to the restricted filling volume of the reactor set-up, for butadiene/glycerol ratios above 4 the overall amounts of glycerol, catalyst, and butadiene had to be reduced to 50 %. Consequently, several parameters potentially changed, including the efficiency of stirring. This effect also complicates the evaluation of our catalytic data because several of the reaction parameters are interconnected and their fully independent variation is difficult to realize. On the other hand,

Table 3. Effect of the butadiene/glycerol ratio on the catalytic activity of Pd/TOMPP as the catalyst in the telomerization of 1,3-butadiene with glycerol.[a]

| Entry | Bu/Gly | $t$ [h] | Conversion[b] [%] | Selectivity[c] [%] | | | TOF[d] [h$^{-1}$] |
|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | |
| 1 | 1 | 0.5 | 48 | 70 | 22 | 8 | 1474 |
| 2 | 2 | 0.5 | 62 | 60 | 29 | 10 | 2780 |
| 3 | 2.5 | 0.5 | 67 | 58 | 29 | 14 | 3040 |
| 4 | 4 | 0.5 | 92 | 39 | 44 | 16 | 5182 |
| 5 | 6 | 0.5 | 23 | 49 | 43 | 8 | 1240 |
| 6 | 10 | 0.5 | 46 | 36 | 55 | 9 | 2626 |

[a] Catalyst concentration = 0.06 mol % [Pd(acac)$_2$] based on glycerol, P/Pd = 5, $T$ = 80 °C. [b] Based on glycerol conversion to glycerol ethers. [c] Based on glycerol ethers. [d] Based on the glycerol conversion to glycerol ethers.

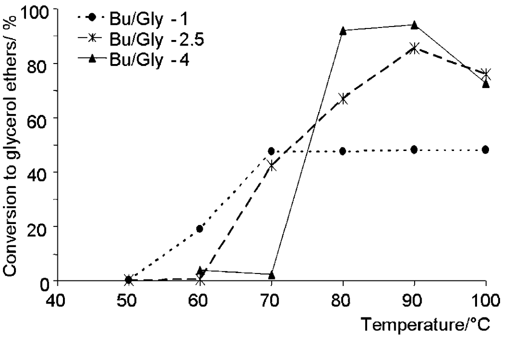


Figure 5. Effect of reaction temperature on the catalytic activity in the telomerization of 1,3-butadiene with glycerol for different butadiene/glycerol ratios (0.06 mol % [Pd(acac)$_2$] based on glycerol, P/Pd = 5, reaction time = 30 min).

for higher ratios of butadiene, palladium black formation could be observed after the reaction. We attribute this catalyst deactivation to a hindered approach of phosphine and/or nucleophile towards palladium.

With regard the product distribution, the highest amount of monoether (70 %) was formed for a butadiene/glycerol ratio of 1. At higher ratios, the amount of monoether decreased, whereas the amounts of di- and triether increased steadily with, for example, 44 % diether and 16 % triether formed in the case of a butadiene/glycerol ratio of 4. This trend even continued for higher butadiene/glycerol ratios. Although the yield and TOF decrease for ratios above 4, a maximum of 55 % diether resulted from a butadiene/glycerol ratio of 10. Surprisingly, at the same time triether formation as low as 9 % was observed. We presume the low yield and conversion at this ratio are responsible for the low triether formation. Although for high conversions the probability of mono- or diethers entering the catalytic cycle as the substrate for further telomerization increases rapidly, at low conversions high amounts of primary alcohols are still available and are, as the primary alcohols seem to react at a higher rate, predominantly consumed, which results in low triether formation at low conversions. Another explanation could be that excess of 1,3-butadiene inhibits the entrance of diethers into the catalytic cycle.

*Effect of reaction temperature:* The reaction temperature was varied for different butadiene/glycerol ratios, with the amount of catalyst and the reaction time kept constant (Figure 5). For all experiments a maximum heating rate was applied to keep the differences in reaction time as small as possible. However, the reactions start before the final reaction temperature is reached. Consequently, for a constant reaction time of 30 min at a given reaction temperature, reactions performed at higher temperatures profit from a slightly prolonged overall reaction time which may result in a somewhat higher activity. Even so, we are convinced that the measured activity profiles reflect the situation very well.

For a butadiene/glycerol ratio of 1, the conversion to glycerol ethers increases from 50 to 70 °C to around 50 % in glycerol. This refers to 100 % conversion in butadiene which is at this point already completely consumed. Accordingly, at higher temperatures no further effects on the conversion are observed. Consequently, the reaction rate appears to be limited by the butadiene concentration for a butadiene/glycerol ratio of 1. For a ratio of 2.5, the temperature dependence of the reaction rate becomes more pronounced, expressed as a steady increase of the reaction yield between 60 and 90 °C, reaching a maximum yield of 86 % at 90 °C. A comparable observation was made for a butadiene/glycerol ratio of 4, for which maximum yields of 92 and 94 % result for reaction temperatures of 80 and 90 °C, respectively. For ratios of 2.5 and 4, the yield drops above 100 °C due to partial decomposition of the catalyst, which forms palladium black in the reaction mixture. Interestingly, the reaction temperature required to reach a significant reaction yield increases with increasing butadiene/glycerol ratio. Whereas for a ratio of 1, 19 % conversion to glycerol ethers is observed at 60 °C, for a ratio of 2.5 very little activity is observed at 60 °C and significant conversion necessitates a reaction temperature above 70 °C. The temperature for significant activity is even higher for a butadiene/glycerol ratio of 4, which shows an even sharper increase above 70 °C, but nearly no activity at this temperature. The sharper increase in activity for ratios of 2.5 and 4 illustrates the temperature dependence of the reaction rate, which becomes more pronounced at higher butadiene/glycerol ratios at which the reaction progress is no longer strongly limited by the butadiene concentration. At the same time, the systems become more and more diluted as the amount of catalyst was kept constant with respect to glycerol. We suggest that, in terms of temperature, the delayed activity in experiments with butadiene/glycerol ratios of 2.5 and 4 is induced by hindered and therefore decelerated catalyst formation in the higher diluted systems, which is compensated by facilitated catalyst formation and higher reaction rates at elevated temperatures. Catalyst decomposition at 100 °C reinforces these suggestions as the activity stayed constant for a butadiene/glycerol ratio of 1 and no palladium black was observed. However, palladium black formation at 100 °C for a butadiene/glycerol ratio of 4 may express the difficulty of the metal centers and ligands forming stable complexes before palladium black formation occurs.

The correlation between reaction temperature and product distribution is presented in Table 4. No clear trend could be observed. Some results indicate a rather high reaction temperature being advantageous for both high yields and high selectivities for mono- and diether formation, as observed in entries 2 and 6 in Table 4.

Table 4. Effect of temperature on the catalytic activity of the Pd/TOMPP catalyst in the telomerization of 1,3-butadiene with glycerol for different butadiene/glycerol ratios.[a]

| Entry | $T$ [°C] | Conversion[b] [%] | Selectivity[c] [%] | | | TOF[d] [$h^{-1}$] |
|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | |
| butadiene/glycerol ratio = 1 | | | | | | |
| 1 | 100 | 48 | 72 | 21 | 7 | 2156 |
| 2 | 90 | 48 | 81 | 16 | 3 | 1850 |
| 3 | 80 | 48 | 70 | 22 | 8 | 1474 |
| 4 | 70 | 48 | 61 | 32 | 7 | 2284 |
| 5 | 60 | 19 | 48 | 35 | 18 | 1080 |
| butadiene/glycerol ratio = 2.5 | | | | | | |
| 6 | 100 | 76 | 71 | 23 | 6 | 3358 |
| 7 | 90 | 86 | 46 | 39 | 14 | 4718 |
| 8 | 80 | 67 | 58 | 29 | 14 | 3040 |
| 9 | 70 | 43 | 76 | 21 | 4 | 1666 |
| butadiene/glycerol ratio = 4 | | | | | | |
| 10 | 100 | 73 | 35 | 25 | 40 | 4430 |
| 11 | 90 | 94 | 37 | 46 | 17 | 5552 |
| 12 | 80 | 92 | 40 | 44 | 16 | 5252 |

[a] Catalyst concentration = 0.06 mol% [Pd(acac)$_2$] based on glycerol, P/Pd = 5, $t$ = 0.5 h. [b] Based on glycerol conversion to glycerol ethers. [c] Based on glycerol ethers. [d] Based on the glycerol conversion in which one catalytic cycle is defined as TON = 1, therefore triether formation requires TON = 3.

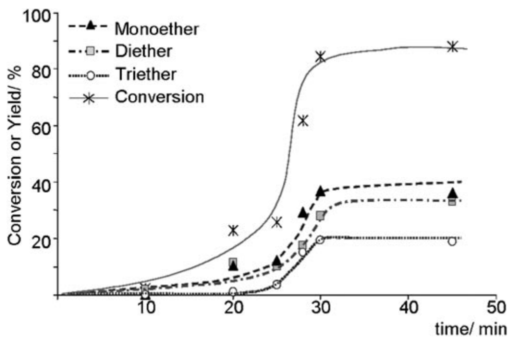


Figure 6. Time-dependent reaction progress of the telomerization reaction for a butadiene/glycerol ratio of 4 (0.06 mol% [Pd(acac)$_2$] based on glycerol, P/Pd = 5, $T$ = 80 °C).

One option that combines high conversion and TOF with high selectivity for mono- and diethers of glycerol could be a shortening of the reaction time. In this regard, Pennequin et al.[10] decreased the degree of substitution of sucrose by reducing the reaction time, which results in a compromise between conversion and degree of substitution. This effect could also be shown for crude glycerol, for which shortening of the reaction time from 1.5 h to 30 min resulted in increased diether and decreased triether formation.[23] Nevertheless, besides variation of the reaction parameters, a deeper understanding of the structure–selectivity dependency is required to allow for directed catalyst development.

*Effect of reaction time*: To evaluate the order of product formation and the effect of base addition on the reaction progress, the reaction mixture was analyzed at regular time intervals. This was performed for butadiene/glycerol ratios of 1, 2.5, and 4. As sampling during the reaction is complicated by the formation of a two-phase system, we decided to perform a new reaction for every data point. Consequently, the deviation between single runs increases, especially for short reaction time. The reaction progress for a butadiene/glycerol ratio of 4 in the time range of 0 to 45 min is presented in Figure 6. Interestingly, in the first 15 min, low conversions are reached, which points to some kind of induction period. This could reflect the hindered catalyst formation suggested for higher dilutions of the reaction system at this butadiene/glycerol ratio. The induction period is followed by a steep increase in conversion between 20 and 30 min reaction time and then a leveling off at around 90% conversion most probably due to complete butadiene uptake. The variation of the product distribution with time emphasizes the fact that primary alcohols of glycerol telomerize more easily. This is reflected by the parallel formation of mono- and diethers in the first 20 min, during which time only a small amount of triether is formed. In addition, the formation of the mono- and diethers proceeds simultaneously, which points towards a comparable activity of glycerol and monoether as substrates in the telomerization reaction. In contrast, a consecutive reaction induced by hindered diether formation should be reflected by the delayed formation of the diether product. Significant triether formation indeed starts only between 20 and 30 min when the reaction proceeds rather quickly, leveling off with the other reaction products after 30 min reaction time. Although sigmoidal curves like those in Figure 6 are well known in palladium-catalyzed C–C bond formation reactions (e.g., the Heck and Suzuki reactions) to be strong indicators of colloidal palladium species as the active catalysts, we could demonstrate by using poisoning experiments that in the telomerization of glycerol with butadiene this is not the case (see above).

The time dependences for butadiene/glycerol ratios of 1 and 2.5 are presented in Figure 7. In contrast to the reaction progress for a butadiene/glycerol ratio of 4, the curves for 1 and 2.5 show less pronounced differences in the induction period, high reaction rates, and a leveling off of the reaction. The delay at the start of the reaction indicates the presence of an induction period followed by a steady progress of the reaction and a leveling off after around 30 min. With regard to the product distribution for a butadiene/glycerol ratio of 1, no remarkable changes were observed. The selectivity for monoether formation remains in the range of 70 to 80%, with 20% diether and around 5% triether being formed (Table 5). For longer reaction times, however, the amount of triether formed increases up to 8%. In the case of a butadiene/glycerol ratio of 2.5, the product distribution changes rather unsteadily as the reaction progresses. In the first

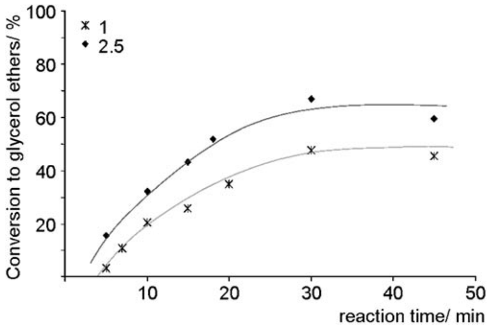


Figure 7. Time-dependent reaction progress of the telomerization reaction for a butadiene/glycerol ratio of 1 and 2.5 (0.06 mol% [Pd(acac)$_2$] based on glycerol, P/Pd = 5, $T$ = 80 °C).

15 min the reaction rate is high and the product distribution shows a maximum for diether formation, which reaches over 50% (Table 5, entries 13 and 14). For longer reaction times, however, the reaction levels off and the product distribution changes again with around 60% mono-, 30% di-, and 10% triether obtained.

Consequently, the simultaneous formation of mono- and diethers of glycerol emphasizes that no consecutive reaction takes place but that both educts, glycerol as well as the monoether, are comparably active as nucleophiles in the telomerization with 1,3-butadiene using Pd/TOMPP as the catalyst system. These results confirm the superior acceptance of sterically demanding nucleophiles by Pd/TOMPP compared with Pd/TPPTS as the catalyst system, for which mainly monoethers are formed with no further telomerization to di- and triethers seeming possible. In this regard, in particular, the formation of triethers of glycerol, which requires the telomerization of diethers as very bulky secondary alcohols, emphasizes the high acceptance of Pd/TOMPP for sterically demanding substrates even in combination with less active functional groups such as secondary alcohols. Therefore, Pd/TOMPP may allow the telomerization of various sterically demanding nucleophiles and will be investigated for potential application in the telomerization of multifunctional nucleophiles such as sugar molecules or secondary amines.

Table 5. Time-dependent development of the product distribution for butadiene/glycerol ratios of 1 (with and without addition of $Et_3N$) and 2.5 in the telomerization of glycerol with 1,3-butadiene.[a]

| Entry | $t$ [min] | Selectivity [%][b] | | | TOF [h$^{-1}$] |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | |
| Bu/Gly = 1 | | | | | |
| 1 | 5 | 70 | 9 | 21 | 938 |
| 2 | 10 | 80 | 16 | 4 | 2523 |
| 3 | 15 | 71 | 23 | 6 | 2278 |
| 4 | 20 | 80 | 17 | 4 | 2137 |
| 5 | 30 | 70 | 22 | 8 | 1474 |
| Bu/Gly = 1 with addition of $Et_3N$ | | | | | |
| 6 | 2 | 94 | 6 | 1 | 2118 |
| 7 | 5 | 78 | 19 | 3 | 6372 |
| 8 | 7 | 76 | 21 | 4 | 5374 |
| 9 | 10 | 68 | 28 | 3 | 4723 |
| 10 | 20 | 72 | 23 | 5 | 2429 |
| 11 | 40 | 75 | 20 | 5 | 1109 |
| Bu/Gly = 2.5 | | | | | |
| 12 | 5 | 59 | 34 | 7 | 4496 |
| 13 | 10 | 27 | 52 | 21 | 6054 |
| 14 | 15 | 23 | 50 | 27 | 5648 |
| 15 | 18 | 60 | 29 | 12 | 4693 |
| 16 | 30 | 58 | 29 | 14 | 3040 |
| 17 | 45 | 63 | 28 | 9 | 1337 |

[a] Catalyst conc. = 0.06 mol% [Pd(acac)$_2$] based on glycerol, P/Pd = 5, $T$ = 80 °C. [b] Based on glycerol ethers.

*Effect of base addition*: To clarify the effect of base addition on product distribution, the conversions to the different reaction products were monitored as a function of reaction time in the presence and absence of $Et_3N$. A butadiene/glycerol ratio equal to 1 was used. The corresponding results are summarized in Figure 8 and show that the reaction starts earlier in the presence of $Et_3N$. In fact, no induction period can be observed compared with the reaction without $Et_3N$ in which the reaction is delayed for about 5 min. Without $Et_3N$ the reaction seems to proceed slightly more slowly, as reflected by a lower slope of the time-dependent reaction curve compared with the reaction performed with $Et_3N$ in the mixture. The faster reaction progress after the addition of $Et_3N$ and the shorter induction period indicate an accelerated formation of the active species. These findings are in close agreement with the explanation of Beller and co-workers[27] and suggest a facilitated reduction of the metal precursor from $Pd^{II}$ to $Pd^0$, which results in a quicker formation of the catalytic active $Pd^0$ species and consequently a reduced induction period.

With regard the product distribution, no significant differences could be observed for reactions performed with and without base (Table 5), which indicates that base addition facilitates the formation of the active species but that $Et_3N$ has no effect on the type of catalytically active species formed and the resulting catalytic cycle.

## Conclusion

Pd/TOMPP complexes are promising catalysts for the telomerization of 1,3-butadiene with glycerol as nucleophile

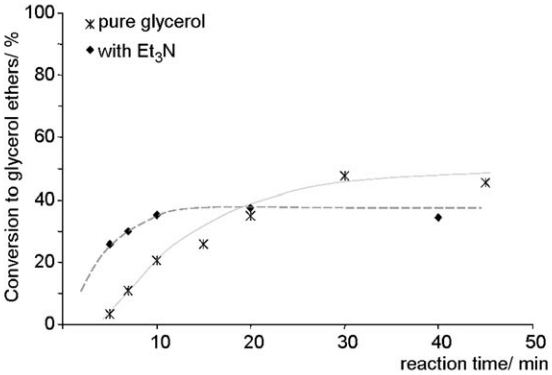


Figure 8. Time-dependent reaction progress with and without addition of $Et_3N$ for a butadiene/glycerol ratio of 1 (0.06 mol% [Pd(acac)$_2$] based on glycerol, P/Pd = 5, glycerol/$Et_3N$ = 10, $T$ = 80 °C).

under various reaction conditions. Two reaction mechanisms involving one- or two-ligand species have previously been proposed for the telomerization of butadiene with methanol.[4,27] Initial attempts to show a comparable mechanism for the telomerization with glycerol have been realized and revealed maximum activities for palladium(0) metal precursors. In addition, the catalytic activity does not depend on the ligand concentration for ligand/metal ratios above two, which points towards a required minimum ligand concentration for significant formation of the catalytically most active species. The first attempts at a rational ligand design aimed at improved selectivities for mono- and diethers were undertaken. The designed system reaches 93 % selectivity for the monoether. The catalytic activity, however, drops significantly compared with the Pd/TOMPP systems and thus further studies of the structure–activity relationship in relation to product distribution and catalytic activity are needed. For the highly active Pd/TOMPP system, the optimization of activity and product distribution depends on several reaction parameters. A maximum reaction rate and yield can be achieved with a butadiene/glycerol ratio of 4 at 90 °C. In terms of a high selectivity for the mono- and diethers of glycerol as target molecules for surfactant applications, lower butadiene/glycerol ratios at high reaction temperatures and short reaction times are beneficial. Addition of $Et_3N$ to the reaction results in a reduced induction period due to a facilitated reduction of palladium to the catalytically active species.

## Experimental Section

In a typical telomerization experiment, $[Pd(acac)_2]$ ($7.5\times10^{-5}$ mol, 22.8 mg) and the triphenylphosphine ligand ($3.75\times10^{-4}$ mol) were added to glycerol (0.125 mol, 11.51 g). The solution was directly mixed inside a 100 mL stainless-steel Parr autoclave and flushed three times with argon. The autoclave was cooled to 258 K using an acetone/dry ice mixture. 1,3-Butadiene was directly condensed in the reactor and the autoclave was heated to the reaction temperature of 353 K and kept there for 5 h or until the pressure had dropped to 1 bar. The starting point of the reactions was defined as the time at which the reaction temperature was reached. After the reaction, the reactor system was cooled to room temperature and flushed several times with nitrogen. The reactor content was analyzed by using a GC 2010 system from Shimadzu with a Supelco-Wax10 column (internal calibration). As none of the reaction products was commercially available, product identification and GC calibration were carried out by column separation of several reaction mixtures. Several fractions were investigated by GC, GC–MS, and $^1H$ NMR measurements, which allowed us to assign the different mono-, di-, and triethers of glycerol and to use the identified clean fractions of the main components for the GC calibration. Branched products were not observed in any $^1H$ NMR spectrum, but cannot be fully excluded. $^{31}P$ NMR measurements were carried out by using $CDCl_3$ as solvent. Butadiene and argon were purchased from Linde Gas Benelux. Chemicals were obtained from Aldrich and were used without any purification.

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[1] E. J. Smutny, *J. Am. Chem. Soc.* **1967**, *89*, 6793.

[2] T. Prinz, B. Driessen-Hölscher, *Chem. Eur. J.* **1999**, *5*, 2069.

[3] T. Prinz, W. Keim, B. Drießen-Hölscher, *Angew. Chem.* **1996**, *108*, 1835; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1708; T. Prinz, W. Keim, B. Drießen-Hölscher, *Angew. Chem.* **1996**, *108*, 1835; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1708;.

[4] F. Vollmüller, J. Krause, S. Klein, W. Mägerlein, M. Beller, *Eur. J. Inorg. Chem.* **2000**, 1825.

[5] F. Vollmüller, W. Mägerlein, S. Klein, J. Krause, M. Beller, *Adv. Synth. Catal.* **2001**, *343*, 29.

[6] R. Jackstell, M. G. Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch, M. Beller, *Angew. Chem.* **2002**, *114*, 1028; *Angew. Chem. Int. Ed.* **2002**, *41*, 986; R. Jackstell, M. G. Andreu, A. Frisch, K. Selvakumar, A. Zapf, H. Klein, A. Spannenberg, D. Röttger, O. Briel, R. Karch, M. Beller, *Angew. Chem.* **2002**, *114*, 1028.

[7] K. Hill, S. Axt, K. J. Weese, WO 9302032, **1993**.

[8] V. Desvergnes, C. Pinel, P. Gallezot, *Green Chem.* **2001**, *3*, 175.

[9] K. Hill, B. Gruber, K. J. Weese, *Tetrahedron Lett.* **1994**, *35*, 4541.

[10] I. Pennequin, J. Meyer, I. Suisse, A. Mortreux, *J. Mol. Catal. A* **1997**, *120*, 139.

[11] B. Estrine, S. Bouquillon, F. Hénin, J. Muzart, *Eur. J. Org. Chem.* **2004**, 2914.

[12] F. Hénin, A. Bessmertnykh, A. Serra-Muns, J. Muzart, H. Baillia, *Eur. J. Org. Chem.* **2004**, 511.

[13] A. Bessmertnykh, F. Hénin, J. Muzart, *J. Mol. Catal. A* **2005**, *238*, 199.

[14] J. N. Cheda, J. A. Dumesic, *Catal. Today* **2007**, *123*, 59.

[15] S. H. Chai, H. P. Wang, Y. Liang, B. Q. Xu, *J. Catal.* **2007**, *250*, 342.

[16] R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angew. Chem.* **2006**, *118*, 4086; *Angew. Chem. Int. Ed.* **2006**, *45*, 3982; R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angew. Chem.* **2006**, *118*, 4086.

[17] A. M. Ruppert, J. D. Meeldijk, B. W. M. Kuipers, B. H. Erné, B. M. Weckhuysen, *Chem. Eur. J.* **2008**, *14*, 2016.

[18] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411.

[19] G. W. Huber, A. Corma, *Angew. Chem.* **2007**, *119*, 7320; *Angew. Chem. Int. Ed.* **2007**, *46*, 7184.

[20] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angew. Chem.* **2007**, *119*, 4516; *Angew. Chem. Int. Ed.* **2007**, *46*, 4434.

[21] D. T. Johnson, K. A. Taconi, *Environ. Prog.* **2007**, *26*, 338.

[22] A. Behr, M. Urschey, *Adv. Synth. Catal.* **2003**, *345*, 1242.

[23] R. Palkovits, I. Nieddu, R. J. M. Klein Gebbink, B. M. Weckhuysen, *ChemSusChem.* **2008**, 1, 193.

[24] a) C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313; b) B. Estrine, S. Bouquillon, F. Hénin, J. Muzart, *Eur. J. Org. Chem.* **2004**, 2914.

[25] S. Borns, R. Kadyrov, D. Heller, W. Baumann, A. Spannenberg, R. Kempe, J. Holz, A. Börner, *Eur. J. Inorg. Chem.* **1998**, 1291.

[26] P. W. Jolly, *Angew. Chem.* **1985**, *97*, 279; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 283.

[27] a) R. Jackstell, S. Harkal, H. Jiao, A. Spannenberg, C. Borgmann, D. Röttger, F. Nierlich, M. Elliot, S. Niven, K. Cavell, O. Navarro, M. S. Viciu, S. P. Nolan, M. Beller, *Chem. Eur. J.* **2004**, *10*, 3891; b) R. Jackstell, S. Harkal, H. Jiao, A. Spannenberg, C. Borgmann, D. Röttger, F. Nierlich, M. Elliot, S. Niven, K. Cavell, O. Navarro, M. S. Viciu, S. P. Nolan, M. Beller, *Chem. Eur. J.* **2004**, *10*, 4661.

[28] K. Kaneda, H. Kurosaki, M. Terasawa, T. Imanaka, S. Teranishi, *J. Org. Chem.* **1981**, *46*, 2356.

[29] W. A. Herrmann, G. P. Albanese, R. B. Manetsberger, P. Lappe, H. Bahrmann, *Angew. Chem.* **1995**, *107*, 893; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 811.

[30] B. Gruber, B. Fabry, B. Giesen, R. Mueller, F. Wangemann, *Tenside Surfactants Deterg.* **1993**, *30*, 422.

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