ELSEVIER

Journal of Molecular Catalysis A: Chemical 197 (2003) 101–113

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Palladium-catalyzed telomerization of butadiene with ethylene glycol in liquid single phase and biphasic systems: control of selectivity and catalyst recycling

Arno Behr*, Michael Urschey

Lehrstuhl für Technische Chemie A, Universität Dortmund, Emil-Figge-Str. 66, 44227 Dortmund, Germany

Received 19 June 2002; accepted 28 October 2002

Abstract

The palladium-catalyzed telomerization of 1,3-butadiene (Bu) with ethylene gylcol (EG) has been studied in liquid single phase and aqueous biphasic systems. All important parameters have been examined, including temperature, catalyst system, catalyst concentration, Bu/EG ratio, P/Pd ratio, solvent and reaction time. In homogeneous phase mixtures of 2-(2,7-octadienyloxy)ethanol (**1a**) and 2-(1-ethenyl-5-hexenyloxy)ethanol (**1b**) were formed in yields up to 60%, but also ditelomers (**2**) and butadiene dimers (**3**) were produced in significant amounts. In aqueous biphasic systems, however, using a palladium catalyst with the triphenylphosphinetrisulfonate (TPPTS) ligand, the monotelomers **1a** and **1b** were obtained in 80% yield with more than 95% selectivity. A mechanism is proposed explaining the observed differences in selectivity. The aqueous catalyst phase could be recycled six times resulting only in a slight decrease of activity. The products **1a** and **1b** were hydrogenated in quantitative yield to the corresponding saturated compounds 2-octyloxyethanol (**6a**) and 2-(1-ethyl-hexyloxy)ethanol (**6b**) using a Pd/Al_2O_3 catalyst under mild conditions. The products can be used for a variety of applications like plasticizers, cosmetics and solvents.

Keywords: Telomerization; Homogenous catalysis; Biphasic catalysis; Butadiene; Palladium

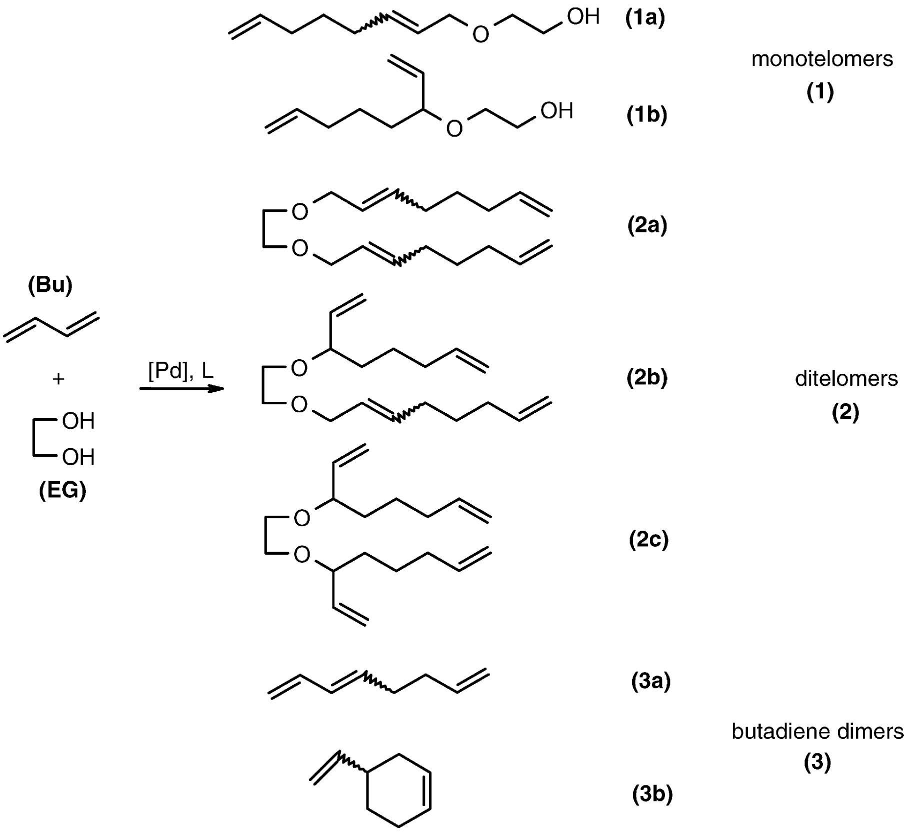
1. Introduction

The telomerization of 1,3-dienes with nucleophiles is one of the most versatile reactions in organometallic chemistry due to the great variability of dienes and nucleophiles which can be used [1]. Since the discovery of the reaction in 1967 by Smutny [2] butadiene has been by far the most widely studied diene while monofunctional alcohols have been examined most extensively as nucleophiles. Recently, a series of papers published by Beller and co-workers reported significant improvements in the industrially interesting telomerization of butadiene with methanol [3–5]. In contrast to monofunctional alcohols and amines, di- and polyfunctional nucleophiles have received much less attention. In the past few years, sucrose has been described as polyfunctional nucleophile, leading to a variety of sucrose ethers [6,7]. Despite these advances, the production of 2,7-octadiene-1-ol starting from butadiene and water is the only industrial application of the telomerization reaction realized so far. A plant is operated by the Kuraray company on a 5000 t per year scale [8]. This reflects clearly the difficulties that are encountered in the selectivity

---

* Corresponding author. Tel.: +49-231-755-2310; fax: +49-231-755-2311.
E-mail address: behr@ct.uni-dortmund.de (A. Behr).

1381-1169/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(02)00599-X



Scheme 1. Telomerization of butadiene with ethylene glycol.

control and the catalyst recycling in telomerization reactions.

The telomerization of butadiene with ethylene glycol (Scheme 1) yields the monotelomers **1a** and **1b** along with the ditelomers (**2**) and the butadiene dimers 1,3,7-octatriene and 4-vinyl-1-cyclohexene (**3**).

The monotelomers (**1**) are of considerable industrial interest as their saturated analogs can be used as plasticizer alcohols for polymers like PVC [9]. Several recent patents are also proof of the industrial interest in these compounds for applications in surfactants and cosmetics [10–12], whereas the ditelomers (**2**) and butadiene dimers (**3**) are of lower interest. Therefore, the control of selectivity is of great importance in order to produce the desired products (**1**) in an atom efficient way. Additionally, for an industrial process to be realized, the recycling of the expensive palladium catalyst is mandatory. The reaction has been described in the literature already in 1980 by Dzhemilev et al. [13] who obtained mixtures of **1**–**3** using a palladium catalyst activated by $AlEt_3$. Kaneda et al. [14] reported a selective reaction to **1a** using homogenous $Pd(PPh_3)_4$ and polymer-bound palladium(0) complexes. However, only a low conversion of ethylene glycol was achieved after a long reaction time of 18 h. Inoue et al. [15] described a recycling method based on the extraction of products by supercritical gases. Yet, the reported reaction yielded a product mixture containing greater amounts of **2** and **3** while the rate and efficiency of product extraction was very unsatisfactory. No procedure yielding efficiently and selectively the desired products (**1**) using a highly recyclable catalyst system has been reported yet. In this paper, we wish to report such a procedure which is based on aqueous biphasic catalysis using an in situ palladium catalyst system. Additionally, an extended mechanism is proposed to explain the observed differences in selectivity. The quantitative hydrogenation of **1a** and **1b** to the corresponding saturated products **6a** and **6b** is also described.

2. Experimental

2.1. Reagents, catalysts and handling

Ethylene glycol (99.5%), 1,3-butadiene (99.5%) and hydrogen (99.999%) were purchased from Fluka and Messer-Griessheim, respectively, and were used without further purification. Dried argon (99.998%, Messer-Griessheim) was used as inert cover gas. Palladiumbis(acetylacetonate)(II) $Pd(acac)_2$ was synthesized according to the literature [16]. Triphenylphosphine (PPh_3; 99%), tri(*n*-butyl)phosphine ($P(n\text{-}Bu)_3$; 95%) and triethylphosphite ($P(OEt)_3$; 97%) were purchased from Acros. Tricyclohexylphosphine (PCy_3; 97%), triphenylphosphite ($P(OPh)_3$; 97%) and sodium hydroxide (p.a.) were purchased from ABCR, Aldrich and Merck, respectively. Triphenylphosphinetrisulfonate (TPPTS) was obtained from Celanese AG as a 25 wt.% aqueous solution of the trisodium salt. Pd/C and Pd/Al_2O_3 catalysts were supplied by Degussa AG. 1,3-Dimesitylimidazoliumchloride (**4**) has been supplied by the workgroup of Prof. Beller at the IFOK Institute in Rostock, Germany. All solvents were degasified and used saturated with argon. All reactions and handling were done under dry argon using standard Schlenk tube techniques.

2.2. Telomerization of butadiene with ethylene glycol in single liquid phase

In a typical experiment, 63 mg (0.2 mmol) $Pd(acac)_2$ and 108 mg (0.4 mmol) PPh_3 were dissolved in 5 ml of THF, mixed in a Schlenk tube with 19.5 ml (0.35 mol) ethylene glycol and transferred into an evacuated 300 ml stainless steel autoclave. Forty-nine grams (0.9 mol) of butadiene were condensed into the autoclave. The vessel was heated to 80 °C and stirred at 800 rpm for 2 h. Consumption of butadiene could be followed by pressure drop from about 10 to about 3 bar. The vessel was cooled to ambient temperature and unreacted butadiene was burnt through a custom-made safety nozzle. The autoclave was opened and a sample of the liquid content taken for GC-analysis. In other experiments, appropriate weighed portions of reagents and catalyst-precursors were used under the stated conditions.

2.3. Biphasic telomerization of butadiene with ethylene glycol

A typical experiment was conducted as follows: 63 mg (0.2 mmol) $Pd(acac)_2$ and 2.3 g (1 mmol) aqueous TPPTS solution were dissolved in 10 ml of deionized water and mixed with 19.5 ml (0.35 mol) ethylene glycol, giving a clear bright yellow solution, which was transferred into an evacuated 300 ml stainless steel autoclave. Forty-nine grams (0.9 mol) of butadiene were condensed into the autoclave. The vessel was heated to 80 °C and stirred at 1200 rpm for 4 h. Consumption of butadiene could be followed by pressure drop from about 10 to about 5 bar. The vessel was cooled to ambient temperature and unreacted butadiene was burnt through the safety nozzle. The autoclave was opened and the biphasic content poured into a separating funnel. One hundred milliliters of cyclohexane were added, the mixture was shaken vigorously and the phases were allowed to separate over a period of 15 min. The lower phase consisting of the aqueous catalyst solution and unreacted ethylene glycol was separated and stored under argon. Cyclohexane was removed from the upper organic phase under reduced pressure (200 mbar, 50 °C) and recycled. The residue was analyzed by GC, Karl-Fischer titration and atomic absorption spectroscopy (AAS) analysis.

2.4. Catalyst recycling

The catalyst solution obtained as described above was supplemented with 1.15 g (0.5 mmol) aqueous TPPTS solution and mixed in a Schlenk tube with 19.5 ml (0.35 mol) ethylene glycol, giving a clear yellow solution that was used for the telomerization reaction as described above.

2.5. Heterogeneous hydrogenation of monotelomer *1a*

In a typical experiment, 5 g (29 mmol) of **1a** were dissolved in 40 ml of THF or cyclohexane and transferred into a 300 ml stainless steel autoclave, which had been charged with 1 g palladium on aluminum oxide (1% Pd on Al_2O_3 pellets, $\varnothing = 2$–3 mm). A custom-made catalyst cage was used to prevent grinding of the catalyst pellets by the stirrer. The vessel was closed, purged with argon and pressurized with hydrogen to 10 bar. The vessel was heated to 70 °C and stirred for 1 h at 800 rpm. Consumption of H_2 could be followed by pressure drop to about 5 bar. Unconsumed hydrogen was vented and a sample of the reaction mixture filtered for GC analysis. In other experiments, appropriate weighed portions of reagents and catalysts were used under the stated conditions.

2.6. Analysis and product characterization

Routine gas chromatographic analyses were done on a HP 6890 instrument (Hewlett-Packard GmbH, Waldbronn, Germany) equipped with a FI-detector and a HP-INNOWax capillary column (30 m, coating polyethylene glycol, diameter 0.25 mm, film thickness 0.25 μm) in connection with an autosampler. GC/MS data were recorded on a HP 5973 instrument coupled with a HP 6890 (30 m HP 5-MS column, coating 5% diphenyl–95% dimethyl-polysiloxane, diameter 0.25 mm, film thickness 0.25 μm) in connection with an autosampler. FTIR spectra were recorded on a Nicolet Impact 400d FTIR spectrometer using KBr plates. NMR spectra were recorded on a DRX 400 spectrometer (Bruker Instruments Inc., Billerica, MA, USA) using $CHCl_3$ as internal standard. Water contents were determined by Karl-Fischer titration on a 652-KF-Coulometer (Metrohm, Herisau, Switzerland). Palladium contents were measured by atomic absorption spectroscopy using an UNICAM SOLAAR 989QZ instrument equipped with a GF90 Zeeman graphite tube oven. All reaction mixtures were analyzed by gas chromatography using external calibration with pure compounds. Products **1a**, **1b**, **2** and **6a** were characterized by IR, standard NMR techniques (^{1}H, ^{13}C, DEPT) and GC/MS. The FTIR and NMR data of compounds **1** and **2** matched the data previously reported [13]. Compounds **3** and octadienols were identified by GC/MS. Octane (**7**) and *n*-octanol (**8**) were identified by comparison of retention times with those of pure compounds and by GC/MS.

3. Results and discussion

3.1. Telomerization reaction in single liquid phase systems

3.1.1. Influence of the reaction conditions

The telomerization of butadiene with ethylene glycol was first optimized in single liquid phase starting from reaction parameters published by Dzhemilev et al. [13] in order to obtain high conversions of glycol and high yields of telomers in short reaction times. The results are summarized in Table 1.

The monotelomers are obtained as a 90:10 mixture of the linear and branched products 2-(2,7-octadienyloxy)ethanol (**1a**) and 2-(1-ethenyl-5-hexenyloxy)ethanol (**1b**), respectively. The monotelomer **1a** consists of about 92% *trans*-compound and 8% *cis*-compound. The ditelomers (**2**) are also obtained as a 90:10 mixture of linear and branched isomers as illustrated in Scheme 1, showing a typical *cis*/*trans* distribution as well. The ratios of linear to branched products and the *cis*/*trans* distributions are not significantly influenced by variation of these reaction parameters. At 120 °C, high yields of telomers are obtained, yet accompanied by rather high formation of butadiene dimers (**3**) (No. 1). Reduction of the reaction temperature to 80 °C affords a strong reduction in dimer formation while achieving similar yields of telomers (No. 2). A catalyst concentration of 0.06 mol% (based on EG) is sufficient to obtain good yields of telomers in 2 h reaction time (No. 3). Lower catalyst concentrations do not yield satisfactory results in short reaction times (Nos. 4 and 5). The P/Pd ratio can be lowered to 2 with some gain of activity (No. 6) while a ratio of 1 results in increased formation of dimers (No. 7). Very low and very high ratios are not productive due to catalyst decomposition (Nos. 8 and 9). Raising the Bu/EG ratio does not significantly increase the telomer yields, but favors formation of dimers (No. 10).

Fig. 1 shows the telomer yields obtained with the standard catalyst system $Pd(acac)_2/PPh_3$ as a function of time. As expected, the reaction is fastest in the first 30 min after which period the yields show a saturation-like behavior due to shortage of the educt EG. The ditelomers (**2**) are formed parallel with the monotelomers (**1**). No typical profile expected for consecutive reactions is found, which will be discussed in detail in Section 3.1.3. These results show

Table 1
Results of the telomerization reaction in single liquid phase

No.	*T* (°C)	Reaction time (h)	Catalyst concentration (mol%)[a]	Bu/EG	P/Pd	Product yield			TON	TOF (h^{-1})[d]
						1 (%)[b]	**2** (%)[b]	**3** (%)[c]		
1	120	2	0.12	2.5	4	60	20	22	675	337
2	80	2	0.12	2.5	4	56	22	5	655	327
3	80	2	0.06	2.5	4	53	18	6	1204	602
4	80	2	0.03	2.5	4	45	10	8	1945	973
5	80	3	0.03	2.5	4	50	9	11	2071	690
6	80	2	0.06	2.5	2	60	23	11	1389	695
7	80	2	0.06	2.5	1	59	21	17	1354	677
8	80	2	0.06	2.5	0.25	Insignificant formation of telomers; partial catalyst decomposition				
9	80	2	0.06	2.5	8	No formation of telomers; catalyst decomposition				
10	80	4	0.06	4.2	2	64	26	27	1501	375

Conditions: catalyst: $Pd(acac)_2 + PPh_3$; 5 ml THF; stirrer velocity = 800 rpm.

[a] Pd-based on ethylene glycol (mol%).

[b] Based on ethylene glycol.

[c] Butadiene dimers in reaction mixture (wt.%).

[d] Average over total reaction time.

that in this telomerization reaction the catalyst system formed in situ from $Pd(acac)_2$ and PPh_3 shows good activity. The addition of a reducing agent like $AlEt_3$ as originally used by Dzhemilev et al. [13] is not necessary, presumably because an excess of phosphine acts as reducing agent to form the catalytically active Pd(0) species. Also, one-fourth of the originally stated Pd-concentration is sufficient to achieve high yields

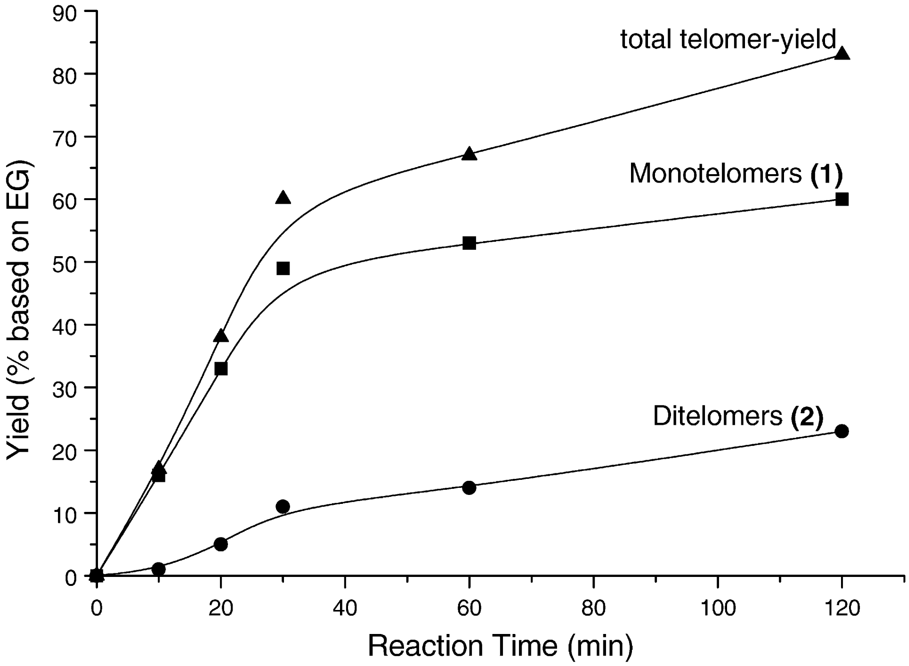
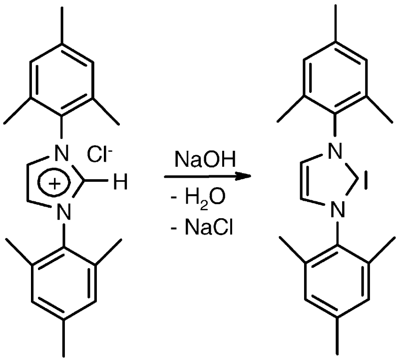


Fig. 1. Yields of telomers achieved with the standard catalyst system under single liquid phase conditions as a function of reaction time, Conditions: catalyst concentration: 0.06 mol% $Pd(acac)_2$ (based on EG); P/Pd = 2:1; 80 °C, stirrer velocity = 800 rpm.

of telomers in 2 h reaction time. TON numbers in the range of 1500 are possible. However, both the catalyst productivity and especially the selectivity to the desired monotelomers (**1**) are unsatisfactory.

3.1.2. *Influence of the ligand*

The influence of several ligands including phosphites, alkylphosphines as well as bis-(diphenylphosphino)alkanes and a *N*-heterocyclic carbene was studied. The alkylphosphines P(n-Bu)$_3$ and PCy$_3$ do not facilitate satisfactory yields of telomers, as do the phosphites P(OEt)$_3$ and P(OPh)$_3$. Instead, high amounts of different dimers (**3**) are formed by catalyst systems incorporating some of these ligands. Obviously, the stereoelectronic properties of these ligands are not suitable for this particular telomerization reaction. Following the idea that it might be possible to influence the selectivity of the reaction by using bidentate ligands with spacer groups of variable length, the four bis-(diphenylphosphino)alkane-ligands DPPM (spacer $= CH_2$), DPPE (spacer $= C_2H_4$), DPPP (spacer $= C_3H_6$) and DPPB (spacer $= C_4H_8$) were tested. Different amounts of THF had to be used in order to solubilize the corresponding catalyst systems. *N*-heterocyclic carbenes (NHC's) have received a revival in recent years due to their unique properties as ligands in catalytically active transition metal complexes. Catalyst systems incorporating NHC ligands were often found to be more active than those incorporating the commonly used phosphine ligands in a variety of C–C coupling reactions [17–20]. Very recently, Beller et al. reported the use of a monocarbenepalladium(0) complex as extremely active catalyst for a telomerization reaction [5]. Therefore, the *N*-heterocyclic carbene 1,3-dimesityl-imidazolin-2-ylidene (**5**) was tested a well. The free carbene ligand (**5**) was generated in situ (Scheme 2) from the corresponding imidazolium chloride salt (**4**).



(4) **(5)**

Scheme 2. In situ generation of carbene ligand (**5**).

The results are summarized in Table 2.

As compared to the monophosphine PPh$_3$, the bidentate phosphines yield a slightly different ratio of **1a**/**1b**, the value being about 95:5. The linearity of the

Table 2
Influence of diphosphine- and carbene ligands on the telomerization reaction

No.	Ligand[a]	Reaction time (h)	Catalyst concentration (mol%)[b]	Bu/EG	Volume THF (ml)	Product yield			TON	TOF (h^{-1})[e]
						1 (%)[c]	**2** (%)[c]	**3** (%)[d]		
11	DPPM	2	0.06	2.5	5	57	25	7	1388	694
12	DPPE	2	0.06	2.5	20	56	16	18	1223	611
13	DPPP	2	0.06	2.5	15	44	5	4	820	410
14	DPPB	2	0.06	2.5	15	22	1	2	389	195
15	DPPP	4	0.06	2.5	15	60	27	13	1467	367
16	DPPB	4	0.06	2.5	15	60	21	7	1367	342
17	**5**[f]	2	0.02	2.5	0	51	41	1	4299	2150
18	**5**[f]	2	0.02	4.2	0	25	75	6	5226	2613

Conditions: catalyst: Pd(acac)$_2$ + ligand; P/Pd = 2:1 or **5**/Pd = 2:1; 80 °C; stirrer velocity = 800 rpm.

[a] See Section 3.1.2.

[b] Pd-based on ethylene glycol (mol%).

[c] Based on ethylene glycol.

[d] Butadiene dimers in reaction mixture (wt.%).

[e] Average over total reaction time.

[f] 1 mol% NaOH (based on Bu) added.

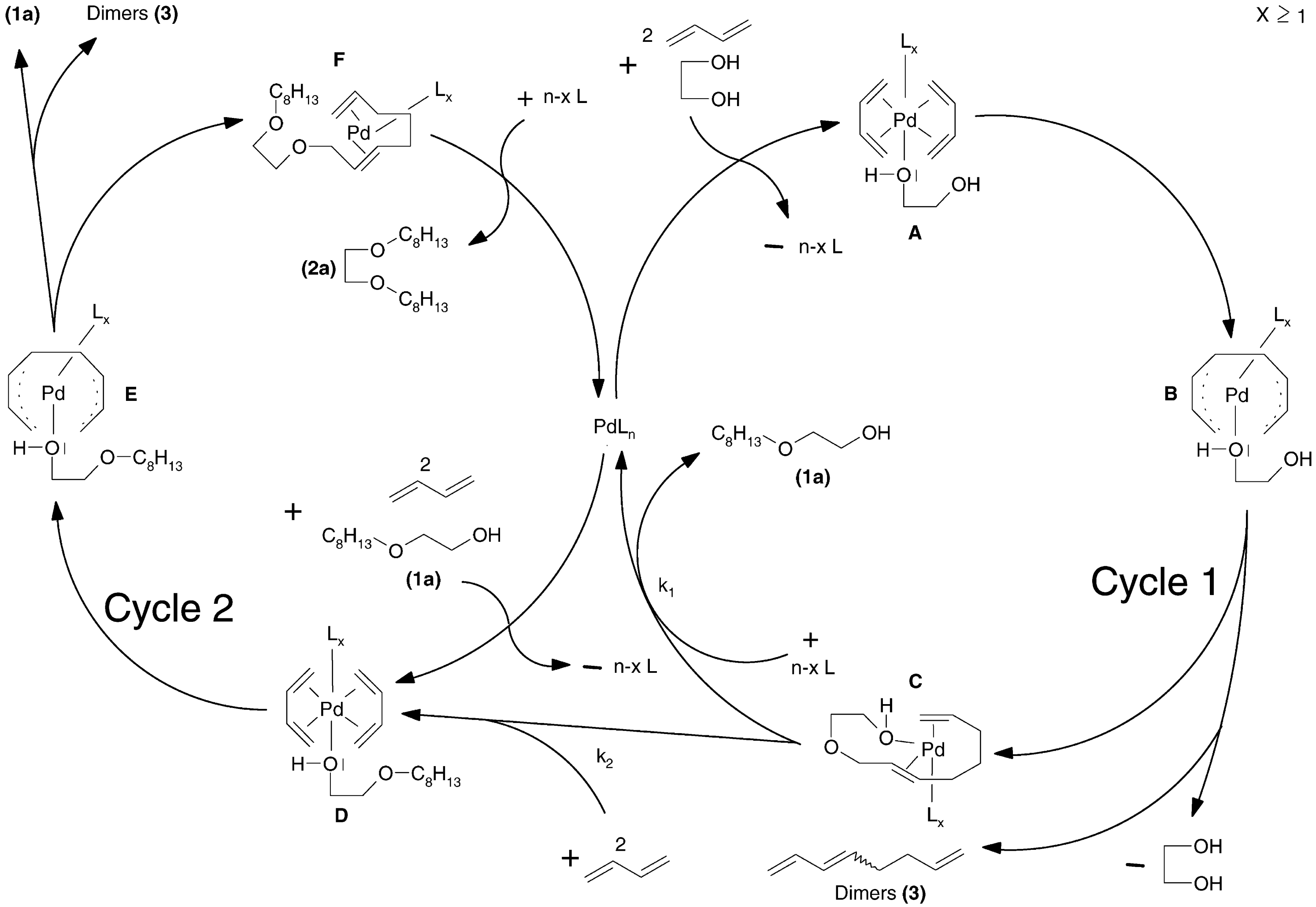
produced ditelomers (**2**) is also increased somewhat (about 94% linear isomers). This effect is explained by the steric bulk of these ligands, which will be discussed in Section 3.1.3. The *cis*/*trans* distributions of the products are not altered. The ligand DPPM performs practically identical to PPh_3 (compare Nos. 6 and 11) which is understood in terms of the instability of the corresponding four-membered chelate complex. The selectivity to the monotelomers (**1**) can be enhanced by using the ligands DPPE, DPPP and DPPB with their longer spacer groups, but the catalyst activity and hence the yield of telomers is decreased (Nos. 12–14). The ligand DPPE yields a rather high amount of dimers (**3**) (No. 12). When longer reaction times are applied with the ligands DPPP and DPPB (Nos. 15 and 16), product distributions and yields similar to those obtained with PPh_3 are observed. The carbene ligand (**5**) gives rise to an extremely active catalyst system offering low formation of dimers and high linearity of the obtained telomers (98% linear products). However, high amounts of ditelomers (**2**) are produced (No. 17). The preference for the ditelomers (**2**) is even more pronounced when the Bu/EG ratio is raised (No. 18). In these experiments, 1 mol% NaOH (based on Bu) is used to deprotonate the imidazolium salt (**4**). Using the carbene ligand (**5**) even much lower catalyst concentrations than used here can be applied as demonstrated by Beller and co-workers [5], making much higher TON's and TOF's possible. However, the maximum alcohol conversion achieved was 25% due to stoichiometric reasons (Bu/alcohol = 1:2). In the present work, higher catalyst concentrations and higher Bu/EG ratios were used to achieve high EG conversions in short reaction times and to maintain comparability with the other experiments. The results show that the selectivity of the reaction can be moderately enhanced in favor of the monotelomers (**1**) by use of bidentate phosphine ligands while higher catalyst activities can be obtained by use of the carbene ligand (**5**) at the expense of lower selectivity to **1**. However, good selectivity to **1** coupled with high activity cannot be achieved following the approaches outlined in this section.

3.1.3. Mechanistic considerations

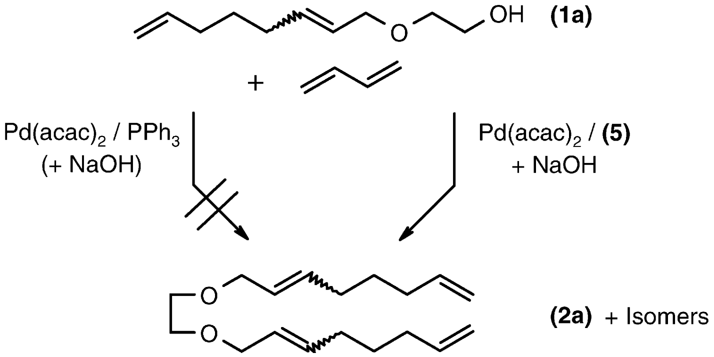
In order to explain the activity and selectivity effects described in the previous sections, an extended mechanism was developed (Scheme 3), which is based on the monometallic mechanism proposed by Jolly and co-workers [21–24]. The formation of branched products like **1b** and **2b** is omitted for clarity, but analogous considerations apply.

In all Pd species, at least one ligand (phosphine or carbene) stays coordinated to the metal center. Starting from the catalytically active species PdL_n (L = ligand) coordination of butadiene and ethylene glycol leads to the intermediate complex **A**, which forms the bis-(η^3-allyl) species **B** by coupling of the butadiene units. Attack of the coordinated nucleophile on the C_8-chain affords the bis-(η^2) complex **C** which eliminates the monotelomers (**1**) under regeneration of the catalytically active species. Intermediate **B** also eliminates 1,3,7-octatriene and ethylene glycol in the dimer forming side reaction. The formation of the ditelomers (**2**) in rather high amounts is somewhat surprising as the monotelomers (**1**) are bad nucleophiles which should not be highly reactive in a consecutive reaction. In fact, the standard catalyst system $Pd(acac)_2/PPh_3$ fails to convert the pure monotelomers (**1**) and butadiene into the ditelomers (**2**) under the usual conditions, even with the addition of NaOH as promoting base. In several control experiments, no formation of **2** was detected (Scheme 4).

Also, Fig. 1 shows that **1** and **2** are produced in parallel at the same time. To explain the formation of the ditelomers (**2**), we propose that a second catalytic cycle (cycle 2 in Scheme 3) is accessible starting from species **C**, which contains a monotelomer (**1**) in coordinated form. **C** can further add butadiene leading to species **D**, which is analogous to **A**, yet still having the monotelomer coordinated. C–C-coupling and consecutive attack of the coordinated nucleophile leads via complex **E** to intermediate **F**, which eliminates the ditelomers (**2**) under regeneration of the catalytically active species. **E** is also subject to the dimer forming side reaction. Catalyst systems incorporating the diphosphines DPPP and DPPB also fail to convert **1** and butadiene into **2**. Therefore, we suggest that the transition from cycle 1 to cycle 2 allows the formation of the ditelomers (**2**) in single liquid phase systems using $Pd(acac)_2$ and phosphines as in situ catalysts. In contrast, a catalyst system with the carbene ligand (**5**) produces **2** from **1** and butadiene in 63% yield under the same conditions, again highlighting its high activity (Scheme 4). Therefore, species **D** is directly accessible starting from PdL_n, **1** and butadiene when this highly active catalyst system



Scheme 3. Proposed mechanism for the telomerization of butadiene with ethylene glycol.



Scheme 4. Conversion of monotelomer (**1a**) to ditelomers (**2**).

is used. Here, a consecutive reaction converting free **1** and butadiene to **2** is possible.

The observed activity and selectivity effects can also be explained with this mechanism. The higher preference for the linear monotelomer **1a** compared to PPh_3 is explained by the steric bulk of the diphosphine ligands, which make it more difficult for the nucleophile to attack the intermediate bis-(η^3-allyl) species **B** in the more hindered three-positions of the C_8-chain. This is also the case when the carbene ligand (**5**) is used. Beller et al. [3] have already established that the regioselectivity in telomerization reactions of butadiene with simple alcohols like methanol is governed by kinetic control. The increasing selectivities to the monotelomers (**1**) and decreasing yields when using the ligands DPPE, DPPP and DPPB (Nos. 12–14) are also attributed to increasing steric bulk in the coordination sphere of the metal, which favors the elimination of **1** from the complex **C**, therefore suppressing cycle 2 ($k_1 \gg k_2$). As the coordination of butadiene and ethylene glycol to the metal is also hindered to some extent, a lower activity results when these ligands are used. The five-membered chelate complex formed from $Pd(acac)_2$ and DPPE (No. 12) is obviously too stable to allow fast attack of nucleophiles on the C_8-chain of intermediate **B**. As a consequence, more dimers are formed with this ligand. With DPPP and DPPB, the transition to cycle 2 is obviously not suppressed over long reaction times as the selectivity to monotelomers (**1**) decreases upon doubling the reaction time (Nos. 13–16). The reason for this may be the decomposition of the ligands. Due to its extremely high activity, the catalyst complex incorporating the carbene ligand (**5**) can form the ditelomers (**2**) both by transition form cycle 1 to cycle 2 and by starting cycle 2 independently from cycle 1.

3.2. Telomerization in aqueous biphasic mixtures

3.2.1. Reactions without supplementation of TPPTS

As demonstrated in the previous section, a highly effective, highly selective reaction to the monotelomers (**1**) cannot be achieved in a single liquid phase reaction as the formation of the ditelomers (**2**) cannot be suppressed to a satisfactory extent. Prinz et al. [25] have demonstrated with their work on the telomerization of butadiene with ammonia that consecutive reactions can be suppressed using aqueous biphasic catalysis. Biphasic catalysis also permits recycling of the homogeneous catalyst. Therefore, the telomerization reaction was carried out in aqueous biphasic mixtures using trisulfonated triphenylphosphine as phosphine ligand. The reaction conditions were adapted to the aqueous medium. A P/Pd ratio of 5:1 was used as lower and much higher ratios lead to fast catalyst decomposition and low yields. The stirrer velocity was set to 1200 rpm to minimize mass transport problems. The results are summarized in Table 3.

The aqueous biphasic reaction is highly selective as only traces of ditelomers (**2**) and dimers (**3**) are formed and a yield of 80% **1** is obtained in 4 h reaction time (No. 19). Only traces of octadienols resulting from nucleophilic activity of the water solvent are found. The highly increased selectivity can be explained by an in situ extraction effect. The aqueous catalyst phase initially contains the Pd/TPPTS catalyst and ethylene

Table 3
Results of the aqueous biphasic telomerization reaction

No.	Recycle	Product yield			TON	TOF (h^{-1})[c]	TTN[d]
		1 (%)[a]	**2** (%)[a]	**3** (%)[b]			
19	Start	80	<0.5	<1	1356	339	1356
20	1	74	<0.5	1	1253	313	2609
21	2	23	<0.5	2	384	96	2993

Conditions: Bu/EG = 2.5:1; catalyst concentration: 0.06 mol% Pd(acac)$_2$ (based on EG) + TPPTS; 10 ml H_2O; 19.5 ml EG; P/Pd = 5:1; 80 °C; 4 h; stirrer velocity = 1200 rpm.

[a] Based on ethylene glycol.

[b] Butadiene dimers in reaction mixture (wt.%).

[c] Average over total reaction time.

[d] Total turnover number.

glycol. The solubility of butadiene is high enough in this phase to facilitate the reaction. The elimination of the monotelomers (**1**) from the intermediate complex **C** is fast ($k_1 \gg k_2$), preventing the formation of intermediate **D** in cycle 2 (Scheme 3). The monotelomers (**1**) are only very slightly soluble in the catalyst phase and separate from the mixture. This also prevents the formation of **D** by direct coordination of butadiene and **1** to the catalytically active species PdL$_n$, which may play a role in single liquid phase systems using highly active catalysts as described above. This way, cycle 2 leading to the ditelomers (**2**) is effectively suppressed. The ratio of **1a**/**1b** and the *cis*/*trans* distribution of the products are not altered compared to phosphine based systems under single liquid phase conditions.

The biphasic reaction permits catalyst recycling. After the reaction was complete, the reaction mixture was allowed to separate into the aqueous catalyst phase also containing unreacted ethylene glycol and the product phase. Cyclohexane was added to achieve a faster phase separation and to remove water from the product phase. The catalyst phase could be recycled with minimal loss of activity (No. 20). In a second recycle, the catalyst lost most of its activity due to decomposition (No. 21). This catalyst decomposition is attributed to the oxidation of TPPTS to the corresponding oxide during the catalytic cycle. This effect has also been observed by Prinz and Drießen-Hölscher [26] in the biphasic telomerization of butadiene with ammonia. A source of TPPTS-oxidation is the contamination with traces of air introduced during work-up of the reaction mixture. Once the P/Pd ratio falls below a critical value, catalyst decomposition results.

3.2.2. Reactions with supplementation of TPPTS

To compensate the loss of ligand, the experiment was repeated and the catalyst phase was supplemented with 2.5 equivalents of TPPTS prior to each recycle run. The results are shown in Table 4.

The reaction could be carried out with excellent selectivity to the monotelomers (**1**) throughout all runs while the activity gradually decreased after the second recycle. After the fourth recycle, catalyst decomposition was becoming evident and the decrease of activity was more pronounced (Nos. 27 and 28). To evaluate the loss of Pd into the organic product phase (leaching), the Pd-concentration in the products was measured by AAS analysis. Typically, 1% of the initially used Pd was lost per run, which is attributed to a residual water content of 0.3 wt.% in the products. The leaching was stronger for the first runs of the series and decreased stepwise towards the end, summing up to about 8% of the initially used metal. Although this degree of leaching is significant, it is not considered the primary cause of the observed loss of activity. Catalyst decomposition plays the major role and can be reduced by supplementation with fresh ligand. This keeps the P/Pd ratio in a favorable range throughout at least seven runs, thereby facilitating effective catalyst recycling. A total turnover number (TTN) of the palladium catalyst in the range of 9000 can be realized. To evaluate the necessary amount of

Table 4
Results of the aqueous biphasic telomerization reaction with supplementation of TPPTS

No.	Recycle	Product yield			TON	TOF (h^{-1})[c]	TTN[d]
		1 (%)[a]	**2** (%)[a]	**3** (%)[b]			
22	Start	74	<0.5	<1	1249	312	1249
23	1	84	<1	<1	1418	354	2667
24	2	83	<1	<1	1393	348	4060
25	3	79	<1	<1	1324	331	5384
26	4	76	<1	<1	1278	320	6662
27	5	68	<1	<1	1145	286	7807
28	6	56	<0.5	<1	936	234	8743

Conditions: Bu/EG = 2.5:1; catalyst concentration: 0.06 mol% Pd(acac)$_2$ (based on EG) + TPPTS; P/Pd = 5:1; TPPTS supplementation: 2.5 equivalents per recycle; 10 ml H_2O; 19.5 ml EG; 80 °C; 4 h; stirrer velocity = 1200 rpm.

[a] Based on ethylene glycol.

[b] Butadiene dimers in reaction mixture (wt.%).

[c] Average over total reaction time.

[d] Total turnover number.

supplementation more exactly, the experiment was repeated and the catalyst phase supplemented with only 1.25 equivalents of TPPTS per recycle. This resulted in catalyst decomposition after two recycles and a TTN of 2900. This degree of supplementation is not sufficient to stabilize the catalyst over a long lifetime.

A patent [27] claims the effectivity of NaOH as activator in biphasic aqueous telomerizations of butadiene with several alcohols. The reaction was carried out with a NaOH/Pd ratio of 8:1 as described in the patent, reproducing all other conditions from the experiment described in Table 4. Very high activity (TOF $> 800\,h^{-1}$; 96% yield) and high selectivity to **1** could be achieved in the initial run, but the formation of octadienols was significantly higher than without addition of base. Also, strong leaching of the catalyst into the organic phase could be observed. Consequently, the activity decreased dramatically in the first recycling run (TOF $< 200\,h^{-1}$; <50% yield). The addition of strong bases to the reaction medium is therefore not suitable for this particular catalyst recycling.

3.2.3. Use of the carbene ligand (5) under aqueous biphasic conditions

The carbene ligand (**5**) was also evaluated for use under aqueous biphasic conditions. The results are shown in Table 5.

Table 5
Results of the aqueous biphasic telomerization reaction using **5** as ligand

No.	Reaction time (h)	Bu/EG	Product yield			TON	TOF (h^{-1})[c]
			1 (%)[a]	**2** (%)[a]	**3** (%)[b]		
29	3	2.5	14	48	2	2889	963
30	4	4.2	15	73	5	4135	1034

Conditions: catalyst concentration: 0.02 mol% $Pd(acac)_2$ (based on EG) + **5**; 1 mol% NaOH based on Bu; 5 ml H_2O; 9.5 ml EG; **5**/Pd = 2:1; 80 °C; stirrer velocity = 1200 rpm.

[a] Based on ethylene glycol.

[b] Butadiene dimers in reaction mixture (wt.%).

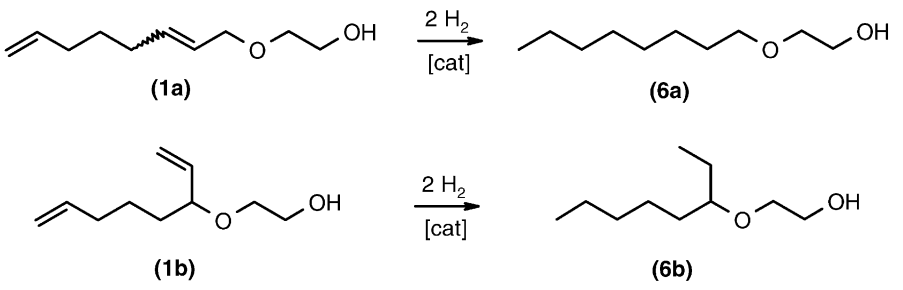
[c] Average over total reaction time.

As compared to water–free conditions (compare Nos. 29 and 30 with Nos. 17 and 18), lower activities and yields of telomers **1** and **2** are achieved. In contrast to catalyst systems incorporating TPPTS, no preference for the monotelomers (**1**) is found. Obviously, the mechanistic phenomena discussed in Section 3.1.3 are also in effect here and the formation of ditelomers (**2**) cannot be suppressed at all. The ratios of linear to branched products are not altered for both monotelomers (**1**) and ditelomers (**2**). While the aqueous medium strongly inhibits the catalytic activity, no significant catalyst decomposition is observed. Due to the neutral nature of the carbene ligand (**5**) strong leaching of Pd into the product phase is observed, which cannot be explained by its low water content of 0.01 wt.%. Therefore, this catalyst system is not suitable for recycling.

3.3. Heterogenous hydrogenation of 1

The hydrogenation of **1a** and **1b** yields the corresponding saturated compounds 2-octyloxyethanol (**6a**) and 2-(1-ethyl-hexyloxy)ethanol (**6b**) which are the products of choice in applications like plasticizers, cosmetics and surfactants (Scheme 5).

For quantitative analysis, the hydrogenation of pure **1a** was studied under mild conditions using standard heterogeneous catalysts. A highly active catalyst (10 wt.% Pd on charcoal powder) and a catalyst of lower activity (1 wt.% Pd on Al_2O_3 pellets) were tested under varying conditions of temperature,



Scheme 5. Heterogeneous hydrogenation of the monotelomers (**1**).

Table 6
Results of the hydrogenation of **1a** using heterogeneous catalysts

No.	Catalyst	T (°C)	Reaction time (h)	Solvent	Product yield		
					6a (%)[a]	**7** (%)[a]	**8** (%)[a]
31	Pd/C	30	0.5	Cyclohexane	80	11	2
32	Pd/C	30	0.5	THF	96	3	1
33	Pd/C	5	3	Cyclohexane	82	10	1
34	Pd/C	5	3	THF	85	13	2
35	Pd/Al_2O_3	30	3	THF	97	0	0
36	Pd/Al_2O_3	70	1	Cyclohexane	100	0	0
37	Pd/Al_2O_3	70	1	THF	100	0	0

Conditions: 5 g **1a**; 40 ml solvent; catalysts: 50 mg Pd/C (10 wt.% Pd on charcoal powder) or 1 g Pd/Al_2O_3 (1 wt.% Pd on Al_2O_3 pellets, $\varnothing = 2$–3 mm); $p(H_2) = 10$ bar; stirrer velocity = 800 rpm.

[a] Based on **1a**.

solvent and reaction time. The results are summarized in Table 6.

Using the highly active Pd/C catalyst hydrogenation is complete within 30 min at 30 °C (Nos. 31 and 32). However, cleavage of **1a** is also observed. The allylic ether functionality of **1a** is sensitive to α-cleavage under reaction conditions, releasing 1-octene (which is quantitatively hydrogenated to octane (**7**)) and *n*-octanol (**8**) as the main products. Though the reaction is more selective in THF than in cyclohexane, total selectivity to **6a** cannot be achieved. At 5 °C hydrogenation occurs much more slowly, but the cleavage reaction cannot be suppressed (Nos. 33 and 34).

Using the less active Pd/Al_2O_3 catalyst hydrogenation occurs almost quantitatively within 3 h in THF at 30 °C without cleavage (No. 35). At 70 °C, hydrogenation is complete within 1 h in either cyclohexane or THF (Nos. 36 and 37), quantitatively yielding **6a**. The same result is obtained within 1.5 h at 50 °C. No cleavage products are observed at all using this catalyst. Likewise, mixtures of **1a** and **1b** can be quantitatively hydrogenated to mixtures of the corresponding saturated compounds **6a** and **6b**.

4. Conclusions and outlook

The palladium-catalyzed telomerization of butadiene with ethylene glycol yielding the valuable ether products **1a** and **1b** has been studied in single liquid phase and aqueous biphasic systems. In single liquid phase systems, high activities could be obtained, especially when the *N*-heterocyclic carbene ligand (**5**) was used in place of phosphine ligands. However, high activity and selectivity to the monotelomers (**1**) as well as catalyst recycling was not possible in these systems. In contrast, a highly selective reaction to the monotelomers (**1**) was realized using aqueous biphasic catalysis and trisulphonated triphenylphosphine. The aqueous catalyst phase could be recycled six times with only slight loss of activity, achieving a total turnover number of the palladium catalyst in the range of 9000. However, both catalyst stability and separation have to be further optimized to make this reaction industrially feasible. It was shown that catalyst systems incorporating *N*-heterocyclic carbene (NHC) ligands can also operate in aqueous media. The synthesis of water soluble carbene ligands might push aqueous biphasic catalysis ahead. Green chemistry standards can be applied to the telomerization process, as the only organic solvent used is cyclohexane which can be easily recycled in a continuous plant. The monotelomers (**1**) could be hydrogenated to the corresponding saturated products **6** in quantitative yield using a Pd/Al_2O_3 catalyst under mild conditions. Other catalyzed follow-up reactions of **1** are currently under investigation. Studies to further improve the productivity of the catalyst system for the telomerization reaction are also in progress. Additionally, the outlined procedures will be extended to other interesting polyfunctional nucleophiles.

Acknowledgements

We thank the Degussa AG for supply of catalysts and the Celanese AG for supply of TPPTS solution and AAS measurements. We also thank the workgroup of Prof. M. Beller at the IFOK Institute for a supply of the imidazolium salt (**4**). We thank Dr. R. Jackstell for valuable discussions. A scholarship from the "Studienstiftung des deutschen Volkes" (MU) is gratefully acknowledged.

References

[1] A. Behr, in: R. Ugo (Ed.), Aspects of Homogenous Catalysis, vol. 5, Reidel, Dordrecht, 1984, p. 3.

[2] E.J. Smutny, J. Am. Chem. Soc. 89 (1967) 6793.

[3] F. Vollmüller, J. Krause, S. Klein, W. Mägerlein, M. Beller, Eur. J. Inorg. Chem. (8) (2000) 1825.

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

[5] 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. 114 (2002) 1028;
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., Int. Ed. Engl. 41 (2002) 986.

[6] K. Hill, S. Axt, K.J. Weese, Telomerization process, WO 9,302,032 (1993).

[7] V. Desvergnes, C. Pinel, P. Gallezot, Green Chem. 3 (2001) 175.

[8] N. Yoshimura, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, Wiley/VCH, Weinheim, 1998, p. 408.

[9] M.G. Romanelli, R.J. Kelly, N.J. Iselin, Verfahren zur Herstellung von ungesättigten Alkoholen, Äthern und Ätheralkoholen, US Patent 2,011,163 (1970).

[10] B. Gruber, K. J. Weese, S. M. Hoagland, H. P. Mueller, K. Hill, A. Behr, Octadienyl ethers and a process for making octadienyl ethers, WO 9,013,531 (1990).

[11] B. Fabry, B. Gruber, Octadienylethersulfate, DE 4,020,973 (1992).

[12] K. Hill, B. Gruber, K.J. Weese, Tetrahedron Lett. 35 (1994) 4541.

[13] U.M. Dzhemilev, R.V. Kunakova, N.Z. Baibulatova, G.A. Tolstikov, A.A. Panasenko, J. Org. Chem. U.S.S.R. 16 (1980) 999.

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

[15] I. Inoue, S. Takeuchi, T. Yamauchi, H. Takita, Method for recovering a catalyst from a homogenous catalytic reaction system, GB 2,054,394 (1980).

[16] G. Künstle, H. Siegel, Verfahren zur Herstellung von palladium(II)acetylacetonat, DE 2,402,383 (1975).

[17] W.A. Herrmann, C. Köcher, Angew. Chem. 109 (1997) 2256;
W.A. Herrmann, C. Köcher, Angew. Chem., Int. Ed. Engl. 36 (1997) 2163.

[18] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. 107 (1995) 2602;
W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem., Int. Ed. Engl. 34 (1995) 2371.

[19] C. Zhang, J. Huang, M.L. Trudeli, S.P. Nolan, J. Org. Chem. 64 (1999) 3804.

[20] C.W.K. Gstöttmayr, V.P.W. Böhm, E. Herdtweck, M. Grosche, W.A. Herrmann, Angew. Chem. 114 (2002) 1421;
C.W.K. Gstöttmayr, V.P.W. Böhm, E. Herdtweck, M. Grosche, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1363.

[21] A. Döhring, P.W. Jolly, R. Mynott, K.-P. Schick, G. Wilke, Z. Naturforsch 36b (1981) 1198.

[22] P.W. Jolly, Angew. Chem. 97 (1985) 279;
P.W. Jolly, Angew. Chem., Int. Ed. Engl. 24 (1985) 283.

[23] R. Benn, P.W. Jolly, R. Mynott, B. Raspel, G. Schenker, K.-P. Schick, G. Schroth, Organometallics 4 (1985) 1945.

[24] P.W. Jolly, R. Mynott, B. Raspel, K.-P. Schick, Organometallics 5 (1986) 473.

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

[26] T. Prinz, B. Drießen-Hölscher, Chem. Eur. J. 5 (1999) 2069.

[27] R. Patrini, M. Marchionna, Process for telomerization of conjugated alkadienes, EP 0,613,875 (1994).