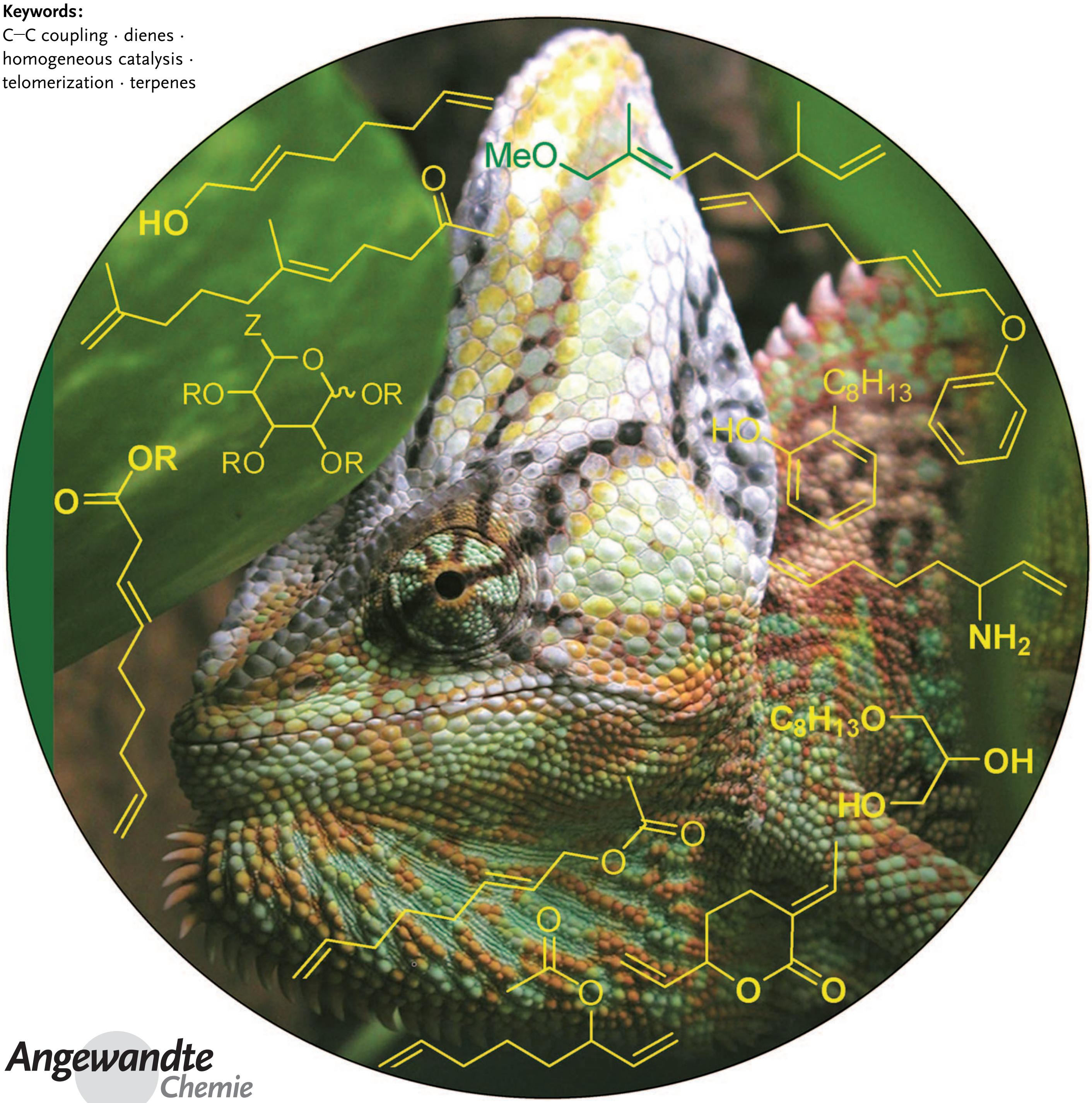
DOI: 10.1002/anie.200804599

Telomerization

Telomerization: Advances and Applications of a Versatile Reaction**

Arno Behr, Marc Becker, Thomas Beckmann, Leif Johnen, Julia Leschinski, and Sebastian Reyer*

Keywords:
C–C coupling · dienes · homogeneous catalysis · telomerization · terpenes

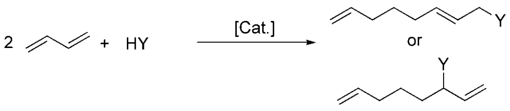


The transition-metal catalyzed telomerization of 1,3-dienes with different nucleophiles leads to the synthesis of numerous products, such as sugar ethers, substituted lactones, or terpene derivatives, which can be applied in the cosmetic and pharmaceutical industry as well as in polymers and flavors. The reaction can be controlled by the choice of the catalytic system, the feedstock, and the reaction conditions. Since telomerization was developed in 1967, there have been many efforts to utilize this reaction. Herein we give an overview of the versatility of telomerization based on examples from research and industry, particular emphasis is placed on catalyst and process development as well as mechanistic aspects.

From the Contents

1. Introduction

If the term telomerization is used in the context of homogeneous catalysis, it refers to the oligomerization of 1,3-dienes (taxogen) under addition of a nucleophilic compound (telogen). An example is given in Equation (1), where the telomerization of 1,3-butadiene with any nucleophile HY containing acidic active H is shown.



(1)

In 1967 this type of reaction was independently discovered by Smutny[1] at Shell and Takahashi et al.[2] from the University of Osaka. The reaction can be catalyzed by various complexes containing transition metals, for example, palladium, nickel, or platinum. Owing to the variety of different dienes and nucleophiles that can be used as reactants in the telomerization, numerous reaction products for countless applications can be obtained. Some of them, such as the telomers formed by the reaction of 1,3-butadiene with water or methanol, are produced on an industrial scale leading to intermediates for the synthesis of plasticizers (1-octanol) or copolymers (1-octene). Other telomers, for example, products of the conversion of butadiene with amines or polyols, are interesting amphiphilic compounds which can be used as surfactants or emulsifiers. Moreover, specialty chemicals such as fragrances or intermediates for the production of pharmaceuticals can be obtained by choosing suitable taxogen/telogen combinations.

As the last extensive Review article was published in 1984,[3] this article will give an overview of the last 25 years of research on telomerization including catalyst development, mechanistic aspects, variety of dienes and nucleophiles, as well as the application of telomerization products. Furthermore, trends in research and possible future applications will be discussed in detail.

2. Mechanisms

2.1. Telomerization with 1,3-Butadiene

The telomerization reaction leads to linear or branched telomers as main products [Eq. (1)]. Furthermore, dimerizations and higher oligomerizations of the diene can take place leading to some by-products. The reaction can be catalyzed by different transition metals, of which palladium is the most important in terms of the number of known reactions and industrially applied processes. In this Section some fundamentals will be discussed.

For palladium there are two different proposed mechanisms for the telomerization reaction depending on the substrates and the catalysts used. The first is the monopalladium bisallyl mechanism (Scheme 1) based on results found by Jolly et al.[4–8] Some intermediates involved in this mechanism were isolated for the reaction of butadiene with methanol. After removal of *n* ligands and oxidative coupling of two molecules of 1,3-butadiene the $[Pd^{II}(^1\eta\text{-}^3\eta\text{-octadiendiyl})]$ complex is formed (steps 1 and 2). The next step (step 3) is the addition of the nucleophilic compound which leads to the C-1 or C-3-substituted octadienylethers (if $Y=OR$) via two intermediates (step 4 and step 5). If no nucleophilic attack takes place, 1,3,7-octatriene is formed in step 4.

The second mechanism found by Keim et al. is the dipalladium bisallyl mechanism (Scheme 2), which was dem-

---

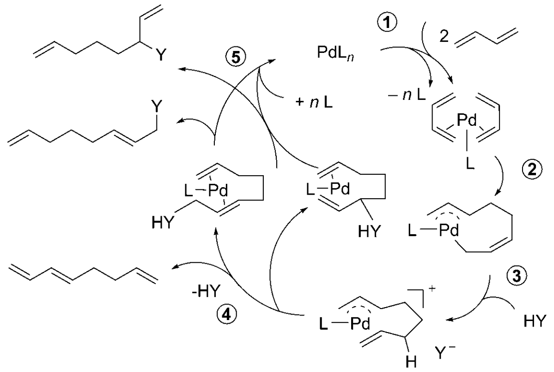
[*] Prof. Dr. A. Behr, Dipl.-Ing. M. Becker, Dipl.-Ing. T. Beckmann, Dipl.-Chem. L. Johnen, Dipl.-Ing. J. Leschinski, Dipl.-Chem. S. Reyer
Department of Biochemical and Chemical Engineering, Technische Universität Dortmund
Emil Figge Strasse 66, 44227 Dortmund (Germany)
Fax: (+49) 231-755-2310
E-mail: behr@bci.tu-dortmund.de

[**] Copyright chameleon: mamboben (http://www.photocase.com/en/)

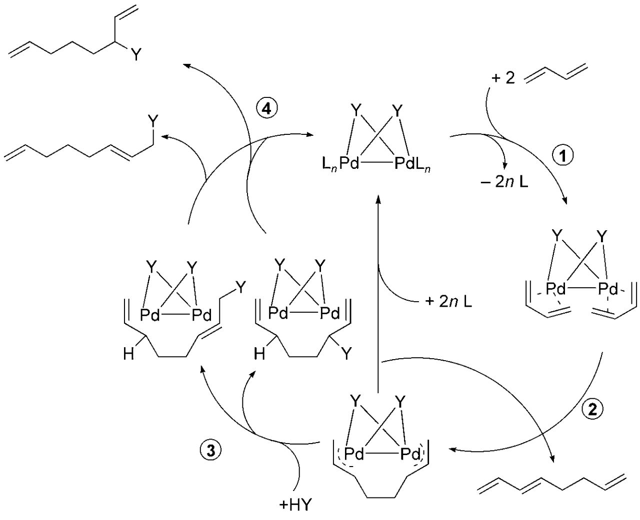
onstrated for the use of phenol or acetic acid as nucleophiles.[9–11] The ligands are dissociated and two butadiene molecules coordinate at the stabilized, bridged-palladium species (step 1), followed by C–C coupling (step 2). In the next step (step 3), the nucleophile attacks at the C-1 or C-3-position, yielding the telomers (step 4). Without nucleophilic attack the dimer 1,3,7-octatriene is formed.

2.2. Telomerization of Isoprene

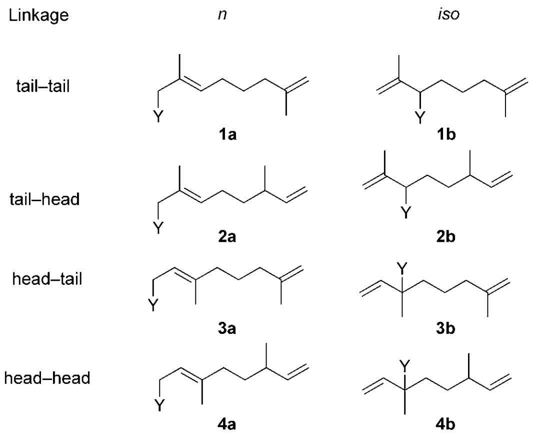
The telomerization of isoprene leads to *n*- and *iso*-telomers as the main products, similar to the telomerization of 1,3-butadiene. The main difference is that isoprene is an asymmetrical 1,3-diene which leads to four different linkages. Each type of linkage can in turn lead to the *n*- or the *iso*-product. Scheme 3 shows the eight types of linkages of isoprene with a nucleophile HY. The *n*-telomers (**1a**–**4a**) of



Scheme 1. Monopalladium-bisallyl mechanism.



Scheme 2. Dipalladium-bisallyl mechanism.



Scheme 3. The different linkages of isoprene.

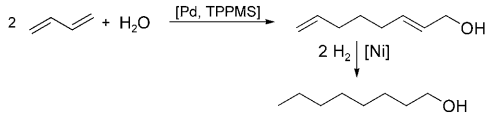
Arno Behr has been the Professor for Industrial Chemistry at the Technische Universität Dortmund since 1996. His research interests cover homogeneous transition-metal catalysis including the development of recycling concepts and the chemistry of olefins and renewable materials. During his PhD studies at RWTH Aachen under supervision of Prof. Wilhelm Keim his research already dealt with transition-metal-catalyzed telomerizations and this reaction is still of major interest in his research group. ***Back row from left****: T. Beckmann, M. Becker, J. Leschinski, S. Reyer.* ***Front row from left****: L. Johnen, A. Behr.*

isoprene are the main products, while the type of linkage differs depending on the reaction system and the nucleophile HY. The mechanistic aspects of the isoprene telomerization are analogous to those described for 1,3-butadiene above. Beller et al. proposed a mechanism for the isoprene telomerization with methanol, which is closely connected to that of 1,3-butadiene with methanol.[12]

3. Telomerization with OH Nucleophiles

3.1. Telomerization with Water

If water is the nucleophile in telomerization, the reaction may also be called "hydrodimerization". The hydrodimerization of 1,3-butadiene with water is still one of the most extensively investigated telomerizations since its products, the octadienols, have a great industrial potential. The octadienols can be easily hydrogenated to 1-octanol, which has a considerable market as raw material for polymer plasticizer (Scheme 4). In 1991, Kuraray implemented the production of 1-octanol on an industrial scale (5000 t a^{-1}).



Scheme 4. Telomerization of 1,3-butadiene with water.

Thereby Kuraray came up with a polar homogeneous catalyst system containing palladium (0) and triphenylphosphine monosulfonate (TPPMS) and thus succeeded in recycling the catalyst, which is dissolved in water/sulfolane and triethylamine (Figure 1). Although these process issues have are already discussed intensively by Yoshimura (from Kuraray),[13] two aspects of the Kuraray process should be discussed in detail at this point.

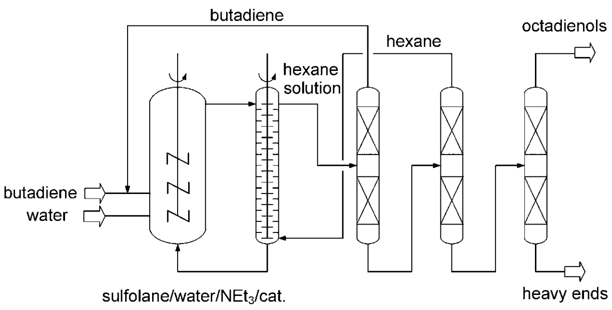
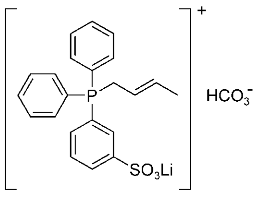


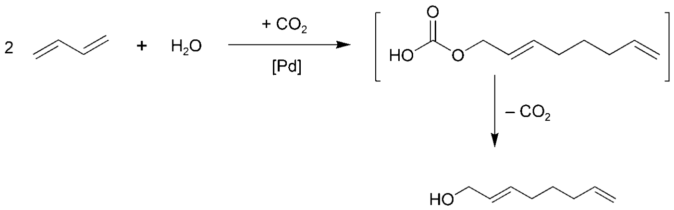
Figure 1. Simplified flow diagram of the Kuraray process.

Kuraray developed an elegant way to adjust the decisive P/Pd ratio.[14] The fact that the activity of the catalyst system decreases dramatically with increasing P/Pd ratio is contrary to the need of excess phosphine ligand to provide sufficient long-term stability. In order to solve this contradiction a tetravalent phosphonium salt **5** is added. This salt of TPPMS is able to form fresh TPPMS successively and thus acts as a catalyst reservoir, which maintains the reaction rate at high level while showing no significant deactivation of the catalyst.



5

The Kuraray process is run under a pressure of 10–20 bar of carbon dioxide. The use of CO_2 has become a common issue in water telomerization since 1971, when Atkins et al. reported the necessity of carbon dioxide assistance.[15] However, the role of CO_2 in water telomerization has not been entirely clarified to date. Monflier et al. assumed that carbon dioxide reacts with water forming carbonates.[16,17] These carbonates are supposed to be better nucleophiles than water and thus form octadienols under elimination of CO_2 (Scheme 5). This assumption is confirmed by the fact that no solvent or CO_2 is needed[18] if telomerization is carried out in the presence of additives such as Na_2CO_3, K_2CO_3, or $KHCO_3$.



Scheme 5. Formation of a carbonate intermediate in water telomerization.

Lee et al. investigated the main influences on the reaction, such as solvent, water/butadiene ratio, or P/Pd ratio.[19] They also described much lower conversion of butadiene and lower selectivity towards octadienol without CO_2 while comparing nitrogen and CO_2 atmospheres (Table 1). These results consider the influence of pressure on the solubility of butadiene in the catalytic phase since both runs were carried out at 200 psi (13.8 bar; Table 1).

Several recent publications deal with the problem of mass transfer between the aqueous phase and the unpolar butadiene phase. Monflier et al.[18] examined the effect of trialkylamines on biphasic water telomerizations. They reported that

Table 1: Telomerization of 1,3-butadiene with water.[a]

CO_2 [bar]	N_2 [bar]	$X_{But.}$ [%]	S [%]	
			2,7-octadien-1-ol	1,3,7-octatriene
0	13.8	34	6	68
13.8	0	78	75	8

[a] $T = 90\,°C$, $t = 1.5$ h, $n_{But.} = 0.25$ mol, $n_{water} = 0.5$ mol, $n_{Pd\ acetate} = 0.5$ mmol, $n_{TPP} = 1.5$ mmol, acetone = 40 mL, But. = 1,3-butadiene, TPP = triphenylphosphine, S = selectivity, X = conversion.

telomerization can be achieved in high yields without additional solvent, as the amines may act like cationic surfactants and thus increase the mass transfer through the formation of micelles. The structure of these amines strongly influences the conversion and selectivity. Monflier et al. also carried out water telomerization s using non-ionic surfactants in a micellar system.[16] They reported an accelerating effect of the neutral surfactants above the critical micelle concentration. The hydrophilic part of the surfactant and the hydrophile–lipophile balance (HLB) have a great influence on the reaction. A third publication from Monflier et al. describes the influence of phosphine/surfactant combinations on the biphasic water telomerization, mainly in terms of electrostatic effects.[17]

Almost all telomerizations described above were catalyzed by palladium(0) and phosphine ligands. Other developments have been made recently. Cermak et al. described the first telomerization in an aqueous biphasic system using nickel(0) complexes.[20] In addition they reported that a high selectivity towards the telomers can also be achieved using palladium(0) complexes and a water-soluble triazaphosphaadamantane ligand. Dullius et al. described hydrodimerization using palladium(II) dissolved in the ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMI][BF_4]).[21] They achieved butadiene conversions up to 28% and selectivity of 94% to the telomer without the presence of CO_2, and in addition a significant increase in conversion (49%) at 5 bar CO_2. Below 5°C the reaction mixture is biphasic, which allows the easy removal of the products and an effective reuse of the ionic catalyst solution.

A completely different approach to water telomerization was chosen by Dehn in our group in Dortmund.[22] Adding the butadiene as a liquid gas usually requires condensing the gas at very low temperatures. For energetic reasons it is therefore more reasonable to provide butadiene as gas under its vapor pressure and to carry out the telomerization as a gas–liquid–liquid reaction. To overcome mass-transfer limitations the telomerization was run in a loop reactor (Figure 2), which assures excellent mixing behavior. For catalyst recycling the liquid–liquid biphasic technique was chosen, which involves continuous separation of the telomer product, whereas the catalytic phase containing a palladium(0)/TPPTS catalyst is fed back into the loop reactor. Thus high space-time yields of octadienols ($35\,kg\,m^{-3}\,h^{-1}$) and low loss of metal catalyst (35 ppm) could be achieved at moderate temperature (60°C) and without the presence of CO_2.

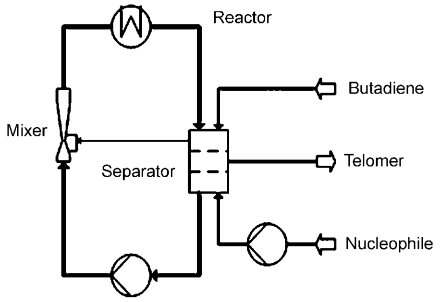


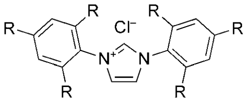
Figure 2. Continuously operated loop reactor for the telomerization.

Owing to its industrial potential, the telomerization with water is widely described in patent literature. At this point two patents are be mentioned by way of example: The Celanese GmbH claimed the use of water-soluble bidentate ligands such as 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl octasulfonate (BINAS) gave higher yields of telomers than with TPPTS.[23] Röper et al. (BASF) described the addition of strong noncoordinating acids such as *p*-toluene sulfonic acid.[24] They assumed that the proton of these acids forms a cation with the allylic system of the butadiene palladium complex, which accelerates the addition of a hydroxy group.

3.2. Telomerization with Alcohols

3.2.1. Monoalcohols

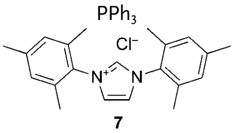
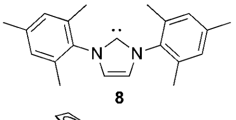
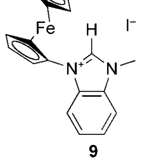
In addition to the telomerization of butadiene with water its telomerization with methanol has been intensively studied. Moreover, an industrial version of this process has been recently established by Dow Chemical Company in Tarragona (Spain). The catalyst system for the industrial reaction is presumed to be the combination of palladium with arylphosphines leading to a yield of 90% methoxyocta-2,7-diene at 70°C.[2,25] The regioselectivity in the telomerization with methanol was improved by the use of in situ generated palladium(0) carbene complexes derived from imidazolium salts (**6**).[26–28]



6

In general, yield, selectivity, and turnover-number (TON) can be increased by using carbene ligands (Table 2). Because of their high performance compared to classical phosphine ligands, carbene complexes are very interesting catalysts for industrial telomerization processes.[29–31]

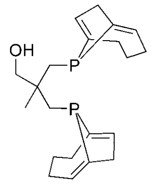
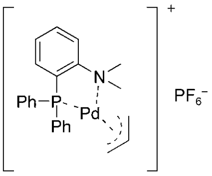
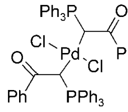
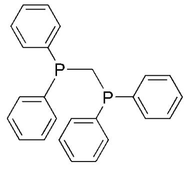
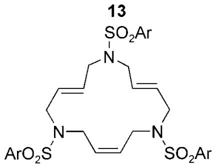
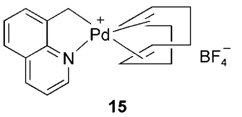
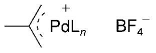
Table 2: Some carbene ligands in comparison to PPh_3.[a] [26]

Ligand	*Y* [%]	*S* [%]	*n*/*iso*	TON
PPh_3	86	92	14:1	86000
 **7**	95	98	35:1	95000
 **8**	92	98	35:1	92000
 **9**	8	75	99:1	8000

[a] $t = 16$ h, $T = 90$°C, 0.001 mol% [Pd(dba)$_2$], Pd/ligand = 1:2; dba = *trans,trans*-dibenzylideneacetone, *Y* = yield.

In addition to the study of carbene ligands there have been several developments and patent applications for the telomerization of dienes with methanol catalyzed by classical phosphine ligands,[32,33] bidentate (or chelate) ligands,[34–37] macrocyclic components,[38] or by cyclopalladated complexes[39] and allylic compounds[40] (Table 3). With macrocyclic compounds, catalyst recovery has been investigated by removing the lower boiling products from the macrocyclic catalyst by distillation. In other cases catalyst recycling is rarely studied.

Table 3: Catalysts for the telomerization of butadiene with methanol.

Ref.	Complex/Ligand	T [°C]	t [h]	$X_{\text{But.}}$ [%]	S [%]
[33]	 **10**	70	0.25	90	>95
[34]	 **11**	60	3	58	96
[35]	 **12**	60	5	51	81
[35]	 **13**	60	4	93	95
[37]	 Ar: 2,4,6-tri-i-propylphenyl **14**	60	1	68	88
[38]	 **15**	60	6	55	21
[39]	 **16**	80	20	100	20

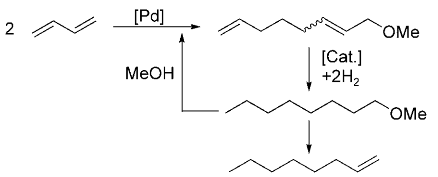
One example for recycling studies is the approach of Chauvin et al. (Celanese). They suggested the use of ionic liquids, for example, [BMMI][Tf$_2$N] (1-butyl-2,3-dimethylimidazolium cation and bis(trifluoromethanesulfonyl)amide anion) in the methanol telomerization[41] to obtain a high selectivity towards methanol telomers together with a low catalyst loss (Table 4).

Table 4: Telomerization of 1,3-butadiene with methanol in the presence of an ionic liquid and different phosphines.[a] [41]

Phosphine	$X_{\text{But.}}$ [%]	S_{Telo} [%]	n/iso	Pd Leaching [%]	TON
TPP	82	53	15:1	14	2127
TPPMS	74	70	13:1	2	1816
TPPDS	56	59	15:1	1,8	1373

[a] $T = 85$ °C, $t = 3$ h, 0.134 mmol Pd, $n_P/n_{Pd} = 3$, $V = 4$ mL [BMMI][Tf$_2$N], 185 mmol MeOH, 10 mL heptane, 370 mmol C_4H_6; TPPDS = Triphenylphosphine disulfonate, Telo. = telomer.

The biggest driving force for the reaction is the production of 1-octene by telomerization (Scheme 6). The classical ways to obtain mixtures with 1-octene are by oligomerization of ethene or by Fischer–Tropsch synthesis. Some companies such as the Dow Chemical Company, Shell, and Oxeno (Evonik) have focused on the reaction sequence shown in Scheme 6[42–44] and Dow has already built a telomerization plant in Tarragona (Spain) to obtain 1-octene as a comonomer for the production of linear low-density polyethylene (LLDPE).



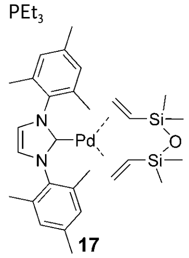
Scheme 6. Production of 1-octene by telomerization.

Owing to the small catalyst concentrations (0.002 mol% relative to 1,3-butadiene), catalyst recycling is unnecessary and thus it is not described in the Dow process,[25] the reaction is presumably carried out with a Pd/PPh$_3$ catalyst system in a plug flow reactor. Further improvement of the cost effectiveness could be made through catalyst recycling, for example, by using the liquid–liquid biphasic technique with a Pd/TPPTS-system. Such a process has already been investigated by Dehn[22] using the continuously operated loop reactor (see Figure 2). As well as obtaining a chemoselectivity of 99% and a regioselectivity for the linear telomer of 95%, very high space–time yields of 105 kg m^{-3} h^{-1} (in 5 h) could be achieved. Long term runs (50 h) showed only minor loss of catalytic activity arising from palladium leaching into the organic phase.

Not only methanol but also other monoalcohols can be converted with dienes. Table 5 shows that the reaction depends decisively on the alcohol. With increasing chain length the amount of unwanted dimers increases and can only be reduced by increasing the ROH/C_4H_6 ratio. Conversion and selectivity are lowered by an increased P/Pd ratio and selectivity is increased by increasing the ROH/C_4H_6 ratio.

The telomerization of isoprene and methanol was intensively studied, mostly by using the standard palladium/phosphine catalyst system. Anderson, Heldt et al. investigated and optimized the telomerization with methanol by calorimetry.[46–49] They also studied the influence of different

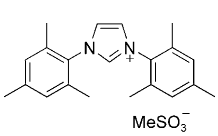
Table 5: Telomerization of butadiene with different alcohols.[a] [28,45]

Alcohol	ROH/ C_4H_6	Pd[b]	Ligand/ Complex	$X_{\text{But.}}$ [%]	$Y_{\text{Telo.}}$ [%]	n [%]
methanol	3:2	0.1	PPh_3	72	93	93
methanol	7:5	0.1	PEt_3	100	98	94
ethanol	9:5	0.1	PEt_3	86	87	97
2-propanol	2:1	0.005	 **17**	100	82	98
1-butanol	2:1	0.001	**17**	100	97	98
1-octanol	3:2	0.2	PEt_3	83	86	96
1-octanol	3:1	0.2	PEt_3	98	91	97
2-methoxyethanol	2:1	0.001	**17**	100	98	98
2-methoxyethanol[c]	3:1	0.2	PEt_3	99	95	96

[a] n = linear, T = 60 °C, t = 2 h, precursor $[Pd(dba)_2]$, solvent n-hexane. [b] mol% relative to C_4H_6. [c] Without solvent.

reaction parameters, such as the catalyst/ligand ratio and the catalyst concentration as well as different phosphine ligands.[46,47] A significant effect was found for the activity of the phosphines used: $PEt_3 > PiPr_3 > PnBu_3 > PCy_3$. The bulky PCy_3 (Cy = cyclohexyl) showed the lowest reaction rates, whereas PEt_3 was the most active ligand. They also investigated the effect of different solvents.[49] In dioxane, THF, and acetone the selectivity for the tail-to-head telomer increased with increasing methanol concentration; a maximum selectivity for the tail-to-head telomer was observed in benzene, toluene, pentane, 2-propanol, and *tert*-butylalcohol. It is remarkable that in ethanol, 2-propanol, 1-butanol, and 2-butanol the selectivities to the tail-to-head telomer increased with lower methanol concentrations. Telomers with alcohols other than methanol were not detected.[49]

Beller et al. used in situ generated carbene ligands in the palladium-catalyzed telomerization of isoprene with methanol. The carbene ligand was 1,3-dimesitylimidazolium mesylate (**18**).[12] The main telomeric product formed was the head-to-head telomer with selectivities between 70–80%. Oligomers of isoprene were also formed with yields of approximately 10% for dimers and approximately 15% for trimers.[12] Other carbene-type ligands were synthesized and tested for isoprene dimerization. Nunes et al. investigated a $Pd(OAc)_2$/carbene catalyst system[50] and also achieved very high selectivities for the head-to-head telomer. The change from the phosphine to the carbene ligands led to a higher oligomerization of isoprene. New sesquiterpenes and new sesquiterpenes containing methoxy groups were produced.[50]



18

Behr et al. studied the palladium-catalyzed methanol/isoprene telomerization and explored several catalyst recycling concepts.[51] The use of a solvent system containing methanol and isoprene gave telomer yields of 43% in 24 h. The products were removed by extraction with 1-dodecene and the catalyst could be recycled together with the methanol (Figure 3).

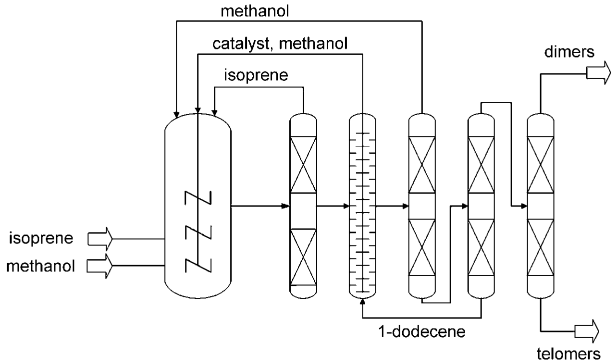
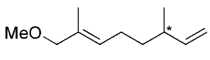


Figure 3. Process concept for the single-phase methanol/isoprene telomerization.

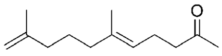
Higher yields of about 50–75% were obtained with a thermomorphic system containing isoprene/methanol/water and a palladium/trisodiumtriphenylphosphinetrisulfonate (Na-TPPTS) catalyst. At a reaction temperature of 60 °C the reaction batch consists of one single phase; when the mixture is cooled down, two phases are obtained. The aqueous phase containing the catalyst could be recycled after cooling the mixture.

Dani et al. studied the chiral telomerization of isoprene and methanol yielding a chiral "tail-to-head" telomer **19**.[52] Several chiral ligands were tested together with different neutral and cationic palladium complexes. The *ee* values obtained of approximately 10% are low.

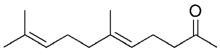


19

The telomerization of isoprene with alkylic acetoacetonates was patented by Keim et al.[53] Different mixtures of protic and aromatic solvents, such as benzene, toluene, phenol, and alkyl phenols were investigated. Palladium acetate with phosphine ligands was used as catalytic system under the addition of a protic component, which could either be one of the protic solvents described above, or alkyl- or arylamines. The desired product is the head-to-tail telomer 6,10-dimethylundeca-5,10-diene-2 one (**20**) because of its structural similarity to α-geranylacetone (**21**).[53]



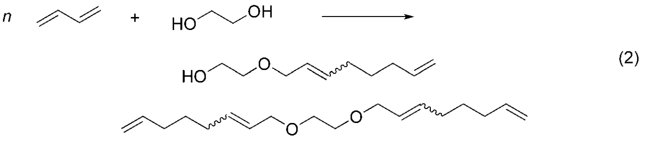
20



21

3.2.2. Polyols

The telomerization with polyols can lead to various products with a different number of ether groups. One example is the telomerization of butadiene with ethylene glycol yielding mono- and ditelomers [Eq. (2)], which has been studied intensively on laboratory and miniplant scale.[54–57]


(2)

The reaction was catalyzed with Pd/TPP or Pd/TPPTS, respectively, in a monophasic or biphasic aqueous system, leading to different selectivities and activities (Table 6). In a further example of the biphasic reaction, ionic liquids can be used to improve product extraction to the organic phase and catalyst recycling within the aqueous phase.[41]

Table 6: Comparison of mono- and biphasic telomerization of butadiene with ethylene glycol.[a] [58]

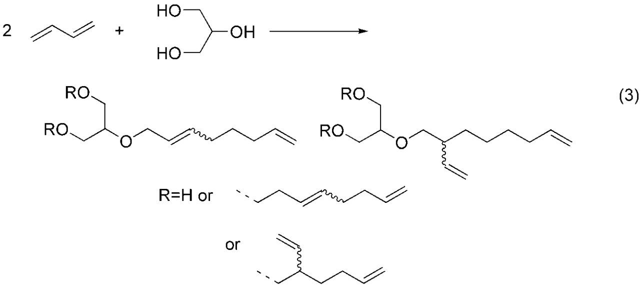
Type	t [h]	Pd/P	Y_{Mono} [%]	Y_{Di} [%]	TON
Monophasic[b]	2	4	53	18	1204
Biphasic[c]	4	5	74	< 0.5	1249

[a] Based on ethylene glycol (EG), $n_{but.}/n_{EG} = 2.5$; 0.06 mol% Pd, $T = 80\,°C$; Mono = monotelomer, Di = ditelomer. [b] 800 rpm. [c] 1000 rpm

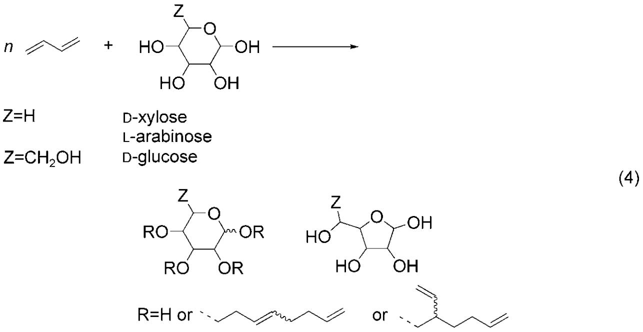
As a result of limited mass transport in the aqueous biphasic system, the stirring velocity and reaction time must be higher than in the monophase system to obtain a comparable TON. The main advantage is the increased selectivity towards the monosubstituted ether, which is a valuable product because of its amphiphilic nature. The monoether hardly dissolves in the aqueous catalyst phase and is therefore not converted into the diether.

Although reactivity of polyols decreases with increasing chain length—as shown by the conversion of propanediols or butanediols—glycerol is an interesting nucleophile for telomerization [Eq. (3)] because it is a by-product of biodiesel production and therefore quite a cheap starting material.[59] In a biphasic system, the selectivity towards the monoether is over 90% as in the case of ethylene glycol, which has led the development of a continuous process for the telomerization of butadiene with glycerol.[60,61] In a miniplant glycerol is converted continuously to glycerol telomers with a selectivity of $S > 90\,\%$ towards the monotelomer.

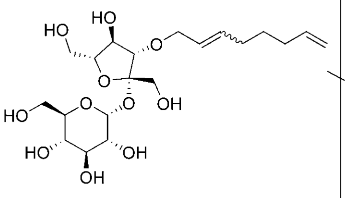
As well as TPP or TPPTS other catalysts have been developed for the telomerization with glycerol. One example is the use of tris(2-methoxyphenyl)phosphine in the monophasic telomerization of crude glycerol which leads to an overall telomer yield of 73% in 1.5 h.[62] However, because there is no mass-transport hindrance the selectivity towards fully substituted tritelomers is quite high ($S = 56\,\%$). Nevertheless, the catalyst system is suitable for crude glycerol, which is a major advantage over other catalysts.

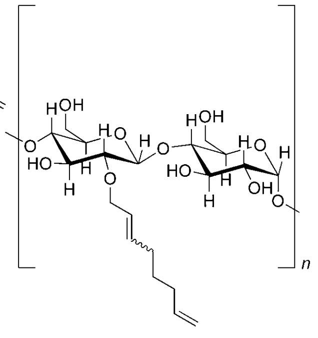

(3)

As renewable starting materials have received more and more attention in the last 25 years, research has also focused on sugars as nucleophiles for telomerization [Eq. (4)]. Mainly aldoses such as xylose, arabinose, and glucose are applied in mono-[63–65] or biphasic reactions,[66] and even substituted sugars such as O-benzylated aldoses can be converted.[67]


(4)

Moreover, higher sugars, such as sucrose,[68–70] or even polycarbohydrates, such as starch,[71] have been converted with butadiene into dienylethers (**22**, **23**).


22


23

Owing to the high number of functional groups, selectivity control is an important issue when using sugars as nucleophiles. As shown in Table 7 the resulting product is always a mixture of mono- and disubstituted ethers as well as higher ethers. The degree of substitution N is defined as the average number of dienyl chains per sugar unit.

With a higher butadiene/sugar ratio and a longer reaction time higher substituted products were obtained as can be seen

Table 7: Telomerization of butadiene with aldoses.[a] [63,66]

Entry	Aldose	t [min]	$n_{\text{But.}}/n_{\text{Ald.}}$	$X_{\text{Ald.}}$ [%]	S [%]			N
					Mono	Di	Tri	
1	D-xylose	15	6	93	78	19	3	1.3
2	D-xylose	60	6	97	68	29	3	1.3
3	D-xylose	60	12	98	44	48	8	1.6
4	L-arabinose	15	6	98	67	31	2	1.4
5	L-arabinose[b]	45	15	96	35	53	12	–
6	D-glucose	15	6	97	62	35	3	1.4

[a] $T = 75\,°C$, 0.7 mol% Pd based on sugar, ligand PPh_3, P/Pd = 2:1, solvent DMF; Ald. = aldose. [b] $T = 80\,°C$, 0.7 mol% Pd based on sugar, ligand TPPTS, P/Pd = 3:1, solvent H_2O/NEt_3

comparing entries 1–3 in Table 7. Furthermore, the choice of sugar has an influence on the selectivity (Table 7, entries 1, 4, and 6). The reaction can also take place in water (Table 7, entry 5). Recycling experiments have shown that catalyst activity decreases as early as the second use.[66]

As well as the use of monosaccharides there has also been research into converting sucrose in a biphasic system. As it is emphasized in Table 8 the choice of solvent, the amount of solvent, and the reaction time have the major influences on the selectivity.

Table 8: Telomerization of butadiene with sucrose in biphasic media.[a] [69]

Solvent	t [min]	$X_{\text{suc.}}$ [%]	S [%]				N
			Mono	Di	Tri	Tetra	
H_2O	300	65	36	48	16	0	1.8
$NaOH_{(aq)}$	23	85	43	45	9	0	1.6
NaOH/*i*PrOH (10/2 v/v)	30	73	66	32	2	0	1.4
NaOH/*i*PrOH (1/2 v/v)	45	98	14	41	38	7	2.2

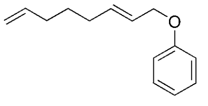
[a] $T = 80\,°C$, P/Pd = 3:1, $c_{\text{NaOH}} = 1\ \text{mol}\,\text{L}^{-1}$.

The conversion of starch as a natural product (80% amylase, 20% amylopectine) was also successful under similar conditions.[71] The reaction temperature must be lower (50 °C) to avoid gelation or catalyst decomposition. The importance of polyols as a feedstock for the telomerization is emphasized by several industrial patents for the production of telomers. They can be used as precursors for the production of surfactants,[72–76] antifoaming agents,[77] or reactive diluents.[78,79] Sometimes it is not even important to purify the starting materials or the reaction products, the whole product mixture can be used as a surfactant. One example is the use of a mixture of wheat bran and straw as a feedstock for the telomerization. The pentoses inside the bran were converted with butadiene leading to a mixture of octadienylethers. This mixture had surfactant properties without further purification or modification.[80] Besides butadiene other dienes, such as isoprene and piperylene, have been patented for the use as reactants in telomerization with polyols but there have been no applications to date.[81–84]

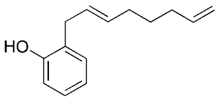
3.2.3. Phenols

Even though phenol was one of the first nucleophiles described in telomerization,[85] there has been very little research into this particular reaction. A possible explanation is the low selectivity, as the telomeric phenoxyoctadienes (e.g. **24**) are always accompanied by *o*- and *p*-octadienylphenols such as (e.g. **25**).

In 1992 Henkel patented the production of sulfonated octadienylarylethers.[72] The first step is the telomerization of butadiene with phenol catalyzed by palladium acetylacetonate and triphenylphosphine. Recent work on telomerization s involving phenols was performed by Beller et al. In telomerizations of butadiene with diverse naphthols and substituted phenols they mainly investigated the formation of C-allylated phenols.[86] Apart from that Vollmüller described telomerizations with *o*-halogenic phenol derivatives such as *o*-chlorophenol or *o*-bromophenol.[87] Chlorophenol showed far more activity in telomerization than bromophenol, which could only be telomerized at temperatures below 0 °C. Beckmann investigated the telomerization of butadiene with phenol using a semibatch operation mode[88] for an aqueous Pd/TPPTS system. All the telomerizations were accompanied by the formation of significant amounts of the by-products octadienylphenol, 1:1-adducts, and dimers. The selectivity could be controlled by the addition of bases, such as sodium phenolate or triethylamine.



24

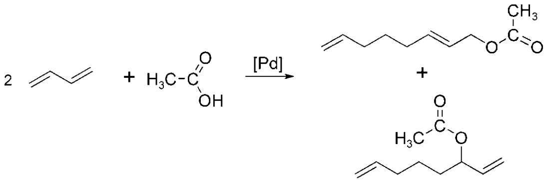


25

3.3. Telomerization with Acids

Although carboxylic acids, especially acetic acid, are well known nucleophiles, their telomerizations have not been investigated since the early work of Walker et al.[89] and Rose and Lepper.[90] The telomerization of butadiene with acetic acid [Eq. (5)] yields acetoxyoctadiene, which can be used as starting compound for the synthesis of various natural and flavoring materials.

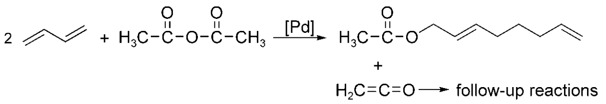
Shell described the telomerization of butadiene with acetic acid as a first step in the preparation of 1-octene in several patents.[91] The following steps of this sequence are



(5)

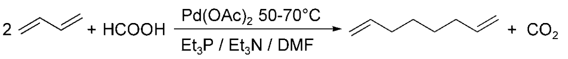
hydrogenation and pyrolysis. Shell also patented the use of a platinum catalyst in the reaction of butadiene and acetic acid.[92]

Recently the telomerization of butadiene with acetic acid was carried out as a gas–liquid reaction[93] with Pd/PPh_3 as the catalyst. In semibatch experiments the reaction requires the presence of a solvent such as 1,4-dioxane. Smaller fractions of acetic acid in the reaction batch gave higher yields of acetoxyoctadiene. In addition, acetoxyoctadiene can be formed in the reaction of butadiene and acetic anhydride [Eq. (6)]. This is the first mention of a telomerization with anhydrides, which do not contain active hydrogen atoms, and takes place as a result of the formation of acetate-bridged bispalladiumcomplexes (see Keim mechanism in Section 2.1). These complexes cleave the acetic anhydride: An acetyl cation is split off, deprotonates to give a ketene, and thus delivers the hydrogen necessary for telomerization.[94]



(6)

The telomerization of butadiene with formic acid[95] yields selectively 1,7-octadiene (96%) under elimination of carbon dioxide [Eq. (7)]. Interest in this reaction has recently increased because 1,7-octadiene is a potential as starting material for the production of 1-octene (Evonik[96]).



(7)

4. Telomerization with Amines

4.1. Telomerization of Butadiene with Amines

Primary and secondary amines have been known as suitable nucleophiles for telomerization for a long time.[2] Early work by various research groups[89,97–100] discovered general trends such as:

- Amines show higher activity with increasing basicity.
- Secondary amines are more nucleophilic than primary ones. Hence, it is generally problematic to obtain secondary amines out of primary amines without forming tertiary amines. Ammonia is less active than primary amines.
- The reactivity of aromatic amines is mostly determined by their substituents.
- Telomerization of secondary amines, which contain long side chains, is limited for steric reasons; for example, dibutylamine is much less active than diethylamine.
- The catalytic activity increases in the series of metals: Ni < Pt < Pd.

Since then, considerable effort has been taken to develop new catalyst systems. Kaneda et al. reported the use of polymer-bound palladium(0)-complexes in the telomerization of butadiene with secondary and primary amines. Of all the investigated substrates morpholine showed the highest activity.[101]

Chernyshev et al. reported an efficient telomerization of butadiene with diethylamine, which was catalyzed by a $[Pd(acac)_2]/BF_3OEt_2$ system (acac = acetylacetonate). The palladium(II) is assumed to react with diethylamine and the boron trifluoride forming $[(acac)Pd(Et_2NH)_2]BF_4$,which is highly active in secondary amine telomerization reactions.[102] Nolan et al. described the telomerization of butadiene with morpholine and other secondary amines using palladium(II) and cationic N-heterocyclic carbene (NHC) ligands. High yields of telomers could be achieved without any catalyst decomposition during the catalytic cycle.[103]

The latest work on telomerization with amines was reported by Beller et al.[104] The telomerization of butadiene with piperidine was chosen as model reaction, which was catalyzed by a NHC-palladium-complex. By using very low catalyst concentrations very high TONs could be obtained. Surprisingly these reactions could be carried out in methanol without forming traces of methoxyoctadiene, the telomer of methanol (see Section 3.2.1). Telomerization of butadiene was also performed with different secondary amines, such as pyrrolidine or dibenzylamine, and primary amines, such as adamantylamine. For all the reactions a NHC ligand provided very high selectivity. Moberg et al. investigated the stereochemistry of the reaction of butadiene with diethylamine. They used a catalytic system containing palladium acetate, triphenylphosphine, and triethylaluminium and obtained extraordinarily high *E*/*Z* ratios when the amount of triethylaluminium was increased. They reported that at a Pd/P/Al ratio of 1/1/2[105] only (*E*)-*N*,*N*-diethyl-2,7-octadienylamine was produced.

The reaction of butadiene with ammonia [Eq.(8)] was studied by Drießen-Hölscher et al.[106–109] To avoid consecutive reactions to the secondary and tertiary amines a biphasic method was chosen, which involves a palladium/TPPTS catalyst, which is retained in the aqueous phase. As shown in Table 9 the selectivity towards the primary and secondary amines could be significantly increased by this approach.

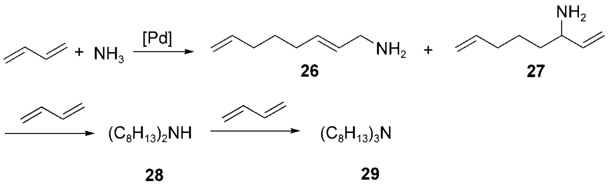
The biphasic telomerization of butadiene with diethylamine was also carried out in ionic liquids for example, in $[BMI][BF_4]$. The optimization of the P/Pd ratio of the polar catalyst system with TPPMS and TPPTS was studied.[110] In recycle runs, a conversion of 65% and a constant high selectivity towards the telomers could be maintained in the first four runs.

The telomerization of butadiene with diethylamine was also carried out as a gas–liquid–liquid reaction[111] using an

Table 9: Comparison of monophasic versus biphasic reactions.[106]

Reaction	*S* [%] **26 + 27**	**28**	**29**
Monophasic[a]	2	4	61
Biphasic[b]	32	26	2

[a] $T = 100\,°C$, $t = 1$ h, $n_{but.}/n_{amm.} = 10$, $n_{but.}/n_{Pd} = 1000$, 20 mL *t*BuOH, $n_{Pd}/n_{PPh_3} = 1{:}3.4$; amm = ammonia. [b] $T = 100\,°C$, $t = 1$ h, $n_{but.}/n_{amm.} = 10$, $n_{but.}/n_{Pd} = 1000$, water/CH_2Cl_2 = 2:1, $n_{Pd}/n_{TPPTS} = 0.25$.

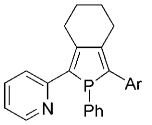


(8)

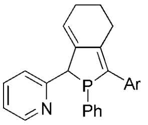
aqueous Pd/TPPTS system. In semi-batch runs a very high selectivity towards telomers (99%) and high space-time yields (112 $kg\,m^{-3}\,h^{-1}$) could be obtained. The catalytic system remained active and could easily be recycled with only a low loss of palladium resulting from removal by the organic phase.

4.2. Telomerization of Isoprene with Amines

The telomerization of isoprene with primary and secondary amines is of great interest especially with diethylamine as a nucleophile. The reason is the structural similarity of the telomers, especially the head-to-tail (ht) product, to natural terpenes. In recent publications the use of aniline as a primary amine is described as well as the use of diethylamine and morpholine as secondary amines. Leca and Réau described the application of new P/N ligands (**30**, **31**) for the palladium-catalyzed isoprene telomerization with diethylamine.[112] They suggested an isomerization reaction of the phospholes **30a–c** to the phospholenes **31a–c** under the reaction conditions. Therefore both types of complexes were synthesized and tested. The similar results of telomer yield (ca. 45%) with each complex type confirm that under the reaction conditions both are present. They also described that the counterion of the palladium precursor as well as an acidic additive have a significant influence on the reaction. When palladium dichloride is used the selectivity of the telomers formed leads towards tail-to-head telomers. The use of cationic palladium complexes gives the tail-to-tail telomers.



30 a–c



31 a–c

Ar = 2-pyridyl (**a**), 2-thienyl (**b**), phenyl (**c**)

Maddock and Finn investigated the isoprene telomerization with diethylamine and morpholine.[113] A significant influence of the palladium precursor and the phosphine ligand were found (Table 10). Triaryl- and trialkylphosphines usually lead to tail-to-head telomers as the major products. This effect is also observed when $[Pd(C_3H_5)(cod)]BF_4$ (cod = cyclooctadiene) was used as a precursor instead of $PdCl_2$. The reaction profile significantly changed when tris(2,4,6-trimethoxyphenyl)phosphine ($P[Ph(OMe)_3]_3$) was used as a ligand in combination with $[Pd(C_3H_5)(cod)]BF_4$. A dramatic increase in selectivity towards the head-to-head telomers was observed forced by the great cone angle of the ligand of 184°.[113]

Table 10: Telomerization of isoprene with diethylamine using phosphine ligands.[a] [113]

Ligand	Precursor	*Y* [%] **1**[b]	**2**[b]	**3**[b]	**4**[b]
PPh_3	$PdCl_2$	21	48	13	18
$P(OEt)_3$	$PdCl_2$	27	47	21	5
PCy_3	$[Pd(C_3H_5)(cod)]BF_4$	29	57	5	10
$P[Ph(OMe)_3]_3$	$[Pd(C_3H_5)(cod)]BF_4$	0	15	1	84

[a] T = RT, t = 40 h, 0.5 mol% Pd based on isoprene, $n_{Pd}:n_P$ 1:1[b] See Scheme 3.

Petrushkina et al. carried out the telomerization of isoprene with aniline. The influence of the catalyst system $[Pd(acac)_2]/PPh_3$ compared to $[Pd(acac)_2]/PPh_3/TFA$ (TFA = trifluoroacetic acid) was investigated in methanol and acetonitrile.[114] It is remarkable that with $[Pd(acac)_2]/PPh_3$ in methanol only telomers were observed while in acetonitrile 1:1 adducts were also formed in yields up to 79%. When TFA was added to the methanol, only 1:1 adducts occurred. In acetonitrile telomers were also formed under these conditions.[114] In further investigations they showed the impact of the ligand, the addition of trifluoroacetic acid, and their ratio on the telomerization of isoprene with aniline.[115] Table 11 shows some selected effects concerning the ligand $P(OEt)_3$. A higher amount of TFA strongly increases the selectivity to the 1:1 adducts and no telomers are formed. Decreasing the catalysts precursor:ligand ratio changed the selectivity towards the telomers.

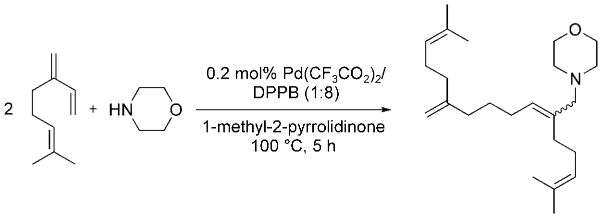
Table 11: Telomerization of isoprene with aniline with different catalyst compositions.[a]

molar ratio of catalyst components[b] $[Pd(acac)_2]/P(OEt)_3/CF_3COOH$	*S* [%] Dimers	1:1 Adducts	Telomers
1:4:10	8	91	0
1:4:4	0	100	0
1:2:4	6	71	23
1:1:4	9	54	37

[a] T = 100 °C, t = 32 h, acetonitrile, n_{Pd} 0.375 mmol, $n_{aniline}/n_{iso.} = 2$; iso. = isoprene. [b] Molar ratio of catalyst components.

In our group, Reyer observed the telomerization of isoprene with piperazine under aqueous, biphasic conditions using a $[Pt(cod)Cl_2]$/Na-TPPTS catalyst system. The catalyst system showed a high sensitivity towards the catalyst:ligand ratio. Ratios above 1:2 only lead to 1:1-adducts, whereas ratios below 1:2 give telomer yields up to 40% with good selectivities to the tail-to-head product.[116]

Recently, Behr et al. reported the formation of the tail-to-tail telomer of myrcene with morpholine in the presence of 0.2 mol% $Pd(CF_3CO_2)_2$/DPPB (1:8; DPPB = bis(diphenylphosphanyl)butane) with a yield of 23% and a selectivity of 88% (Scheme 7).[117] This was the first report of the telomerization of the triene myrcene.



Scheme 7. Telomerization of myrcene with morpholine.

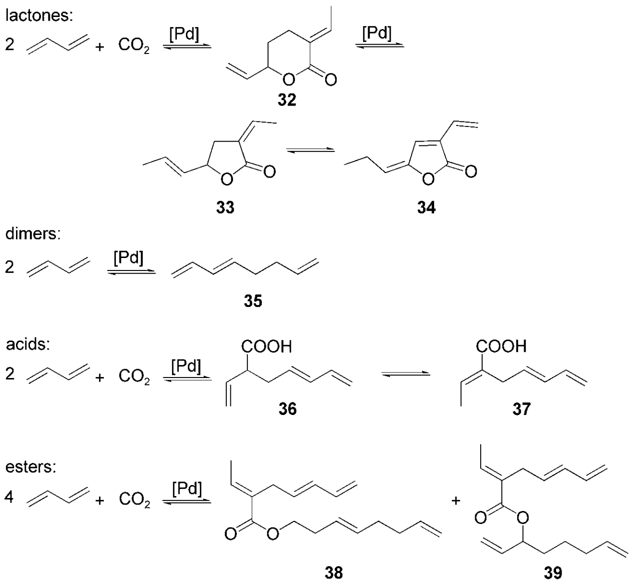
5. Telomerization with Carbon Oxides

5.1. Telomerization of Butadiene with CO$_2$

The first studies of the telomerization reaction of 1,3-butadiene with carbon dioxide were carried out by the research groups of Inoue[118] and Musco.[119] They succeeded in synthesizing lactones (**32**–**34**), 1,3,7-octatriene (**35**), carboxylic acids (**36**, **37**), and esters (**38**, **39**) in small quantities. In the following years Braunstein et al.[120,121] and Behr et al.[9,122,123] examined the telomerization leading to the δ-lactone (2-ethyliden-6-hepten-5-olide, **32**) in detail (Scheme 8).

Dinjus et al.[124] reported the telomerization of butadiene in supercritical carbon dioxide when using nitrile-modified phosphine ligands which form the active catalyst with palladium(0) in situ. During reaction times of 20 h and temperatures of 60–80 °C conversions of butadiene from 70–90 % with δ-lactone selectivities up to 47 % were achieved. Holzhey et al.[125–127] described the use of immobilized polymer-bound phosphines and a palladium species for improved catalyst recycle. In 18 h a maximum of 48 % conversion and 11 % yield of δ-lactone were reported at temperatures of 70–80 °C. During recycling experiments the catalyst activity dropped to 12 % conversion.

Intense research and catalyst screening[123,128–132] showed that only palladium catalysts, preferably [Pd(acac)$_2$] led to significant yields of δ-lactone. By use of tricyclohexylphosphine (PCy$_3$) as ligand, selectivities up to 95 % for δ-lactone could be achieved in 15 h reaction time. Based on the batch laboratory results with the catalyst system [Pd(acac)$_2$]/PCy$_3$ a process for a continuous miniplant was developed by Heite and Behr[133,134] using an extraction unit to recycle the homogeneous catalyst. However, during continuous operation of the miniplant the extraction media 1,2,4-butanetriol lead to deactivation of the catalysts. To separate the product, Ebbers and Behr[135] integrated an evaporation step instead of the extraction into the miniplant (Figure 4). The catalyst could be recycled together with small parts of the liquid product to give a constant yield of the δ-lactone of about 20 %.



Scheme 8. Products obtained by telomerization of butadiene with CO$_2$.

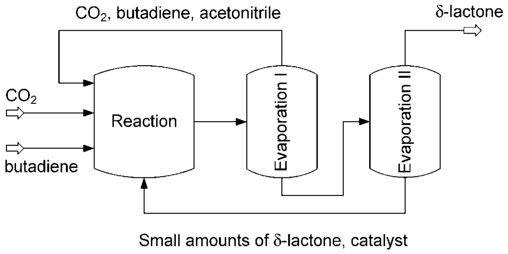


Figure 4. Process for the telomerization of butadiene with CO$_2$.

Bahke[136] examined the use of the ligand PPh$_3$ and showed its high potential in the telomerization of butadiene and CO$_2$. As Table 12 shows, with PPh$_3$ better yields of δ-lactone were achieved under the same reaction conditions as for PCy$_3$, however, at significantly lower selectivities. By reduction of the reaction time the yield of δ-lactone was enhanced by factor two compared to PCy$_3$ reaching a selectivity of 71 %. The yields of dimer **35** stayed relatively low with yields of 2–3 %. Further studies concentrated on the optimization of the catalyst system [Pd(acac)$_2$]/PPh$_3$.[136] The molar ratio of butadiene to CO$_2$ was identified as a crucial reaction parameter. The results of the laboratory batch experiments were used for a miniplant run over 70 h.[137] During the whole miniplant run a constant product stream of 8 g h^{-1} was obtained with an overall yield of 30 % and a selectivity of 80 % while the heavy-end by-products (**36**–**39**) did not accumulate in the reactor. A total number of nine recycles was achieved during 60 h of continuous operation and no catalyst deactivation was observed.

Table 12: Influence of the ligands PCy$_3$ and PPh$_3$ ($T = 80$ °C).

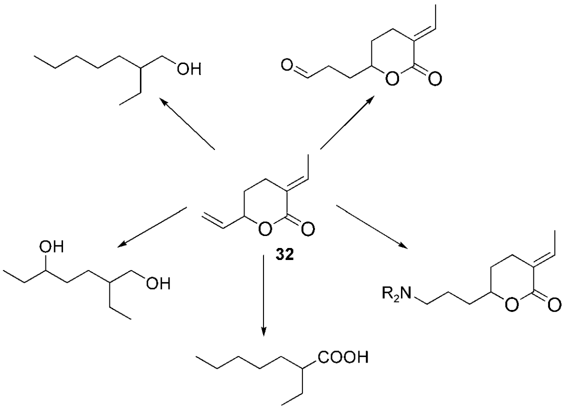
[Pd(acac)$_2$] [mmol]	Ligand [mmol]	t [h]	$X_{\text{But.}}$ [%]	Y(**32**) [%]	S(**32**) [%]
0.4	PCy$_3$ 1,2	15	21	17	81
0.4	PPh$_3$ 1.2	15	95	23	24
0.4	PPh$_3$ 0.8	6	51	36	71
0.05	PPh$_3$ 0.15	6	24	19	77

Further investigations regarding alternative solvents[136] showed that the cyclic carbonates ethylene, propylene, and butylene carbonate are highly active giving yields of δ-lactone up to 45 % with a selectivity of 88 %. The reaction time could be further reduced compared to acetonitrile from 6 h to 4 h (Table 13).[138] Some of the numerous derivatives of the δ-lactone are shown in Scheme 9.

Table 13: Comparison between acetonitrile and carbonate solvents.[a]

Solvent	$X_{But.}$ [%]	Y(**32**) [%]	S(**32**) [%]
acetonitrile	73	28	38
ethylene carbonate	52	45	88
propylene carbonate	69	44	64
butylene carbonate	88	33	37

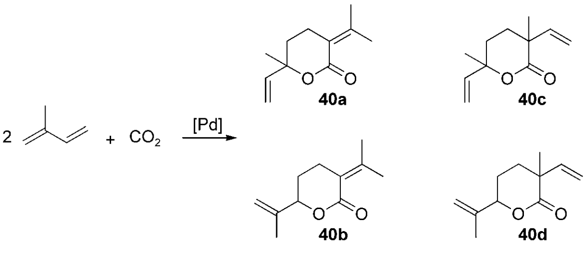
[a] [Pd(acac)$_2$]/PPh$_3$, 4 h, 80 °C.



Scheme 9. Derivatives of the δ-lactone **32**.

5.2. Telomerization of Isoprene with CO$_2$

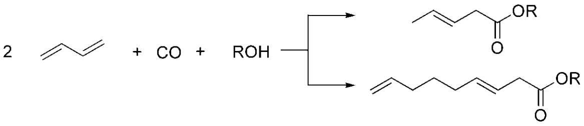
Dinjus and Leitner[128] examined the telomerization of isoprene with carbon dioxide. In contrast to the reaction with butadiene, quantitative conversion of isoprene could not be achieved. During 20 h reaction time at 90 °C using [Pd(acac)$_2$]/dicyclohexylphosphinobutane (DCPB) as catalyst an overall yield of the isomers **40 a–d** (Scheme 10) of only 1 % was obtained.



Scheme 10. Products obtained by telomerization of isoprene with CO$_2$.

5.3. Carboxy-Telomerization

A telomerization can also proceed with additional incorporation of carbon monoxide. This so-called carboxy-telomerization yields, for instance, nona-3,8-dienoates based on butadiene and an aliphatic alcohol (Scheme 11).



Scheme 11. Monomeric and dimeric carbonylation of butadiene; R = alkyl group.

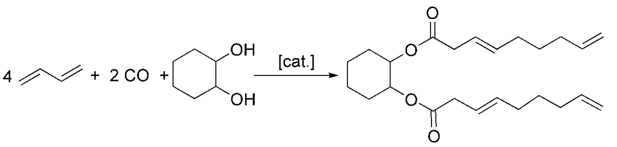
The alkyl 3,8-nonadienoates are useful starting materials for several derivatives. After hydrogenation, for instance, the methyl pelargonate can be used as flavor or fragrance because of its characteristic odor of wine and coconut. It can also be a useful compound in making the corresponding pelargonic acid for the synthesis of brake fluids and surfactants. The hydrolysis yields nonanol, which is an intermediate in the plasticizer industry or used in the manufacture of artificial lemon oil. Additionally, the nonadienoate serves as interesting starting material for "royal jelly acid", the 10-hydroxy-2-decenoic acid—a compound appreciated for its skin care and antibacterial effect in health food or cosmetics.[139]

Romanelli applied for a patent describing a homogeneous catalyzed preparation of alkadienoic acid esters.[140] Former reports already indicated that palladium catalysts are effective in the carbonylation of dienes.[141,142] Therefore it was apparent that palladium catalysts were the right choice for carrying out a dimerization of conjugated aliphatic diolefines followed by a carbonylation and esterification. Romanelli used the palladium complex [Pd(acac)$_2$] in combination with the monodentate triphenylphosphine to give the alkadienoic acid esters with yield up to 80 %. Independently, Billups et al. described the same results using the same catalyst systems.[143] They found that if ethanol is used the major by-product is ethoxyoctadiene.

Tsuji et al. reported that the presence or absence of a halide ion coordinated to the palladium represents an essential factor in the differentiation of monomeric and dimeric carbonylations (Scheme 11).[144] In contrast, the steric bulk of the alcohols is less important. For instance, the bulky *t*BuOH gives the corresponding ester analogue to ethanol. In contrast, the carbon monoxide pressure has much more effect on the reaction: A higher pressure decreases the yield, for example, a doubling of pressure of 50 to 100 bar reduces the yield from 90 % to 30 %.

Further work deals primarily with additives improving the performance or with other solvents stabilizing the palladium catalyst because in early syntheses precipitation of palladium metal and low solubility of the [Pd(acac)$_2$] precursor in butadiene complicated the realization. Knifton introduced tertiary amine solvents which have a moderate base strength to improve the solubility of the palladium precatalyst and even to enhance ester yields.[145,146] Foley used thiol compounds as stabilizers for the catalyst system [Pd(acac)$_2$]/P*i*Pr$_3$ (1:2) in the presence of hydrochinone giving small amounts of thioesters as by-products.[147] The same catalyst system can be stabilized with maleic anhydride as reported by Kiji et al.[148] With this catalyst system Vanderspurt and Zema succeed in the first realization of an efficient catalyst recycling using the biphasic technique.[149] The reaction is conducted with methanol, a hydrocarbon solvent, such as pentane, and in the presence of small amounts of water. After 15 h in the presence of 63 bar CO, 94 % of the nonadienoate is obtained. During the course of reaction the mixture is one liquid phase, after cooling to 5 °C two phases are formed caused by a temperature-dependent miscibility gap of methanol/water/pentane. Only very polar alcohols, such as methanol or glycol, have a miscibility gap, so that this process is only feasible with these kind of alcohols.

Further investigations by Schöbel in our group concerning catalyst recycling by the two-phase technique indicate that conventional water-soluble ligands as mainly the triphenylphosphinetrisulfonate are not effective in a liquid–liquid biphasic system, probably because of their lower basicity.[150] As an alternative concept Schöbel uses thermomorphic fluorinated solvent systems. The fluorinated solvents are not miscible with most organic solvents at ambient temperature, but pass into one single phase at higher temperature. The use of cyclohexandiol as a nucleophile affords, after hydrogenation, a telomeric product, which is comparable to the phthalic esters used as plasticizers [Eq. (9)]



(9)

6. Telomerization by Heterogeneous Catalysts

As described above, homogeneous palladium catalysts have been extensively investigated because of their high activity and selectivity. Heterogenized catalysts may appear to be more attractive from the industrial point of view, especially because the catalyst may be easily separated from the reaction products and recycled. A change to a heterogeneous system can also be essential, when high-boiling points of the reaction products require high temperatures for separation by distillation, and thus cause a damage of the homogeneous catalyst.

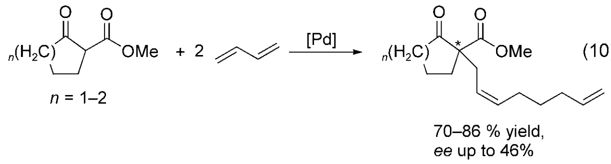
Lazutkin et al. chose silica and tin acetate as the inorganic linker with which to build the backbone to heterogenize the π-allyl palladium catalyst.[151] The supported palladium–tin catalyst with palladium concentrations up to 2 % shows a high activity and stability, giving up to 90–95 % butadiene conversion in the telomerization with diethylamine at 20 °C. However, recycling experiments to check the immobilization of the catalyst are still required. Benvenuti et al. also used activated silica to support the precursor [Pd(acac)$_2$].[152] But various recycling experiments in the telomerization of butadiene and methanol and the determination of Pd amounts in the product phase demonstrated that the activity observed is fully related to the palladium content in the solution.

In the telomerization with water[153] Lee et al. reported that the use of palladium anchored on montmorillonite shows good activity and selectivity towards octadienol. After the reaction the solution contains less than 1 % Pd. When Pd-montmorillonite was separated from the liquid products by filtration and then reused as the catalyst under the same conditions, the same activity and selectivity of the first run was achieved verifying the heterogeneous properties.

Estrine et al. applied [Pd(tppts)$_n$], which is a classical catalyst system for biphasic techniques, heterogenized on montmorillonite, silica, and KF/alumina.[154] The palladium catalyst heterogenized on KF/alumina gives the best preservation of activity and selectivity over four recycling runs in the telomerization of butadiene and methanol. Using the same catalyst system the telomerization of butadiene can also be conducted with phenol and D-xylose [see Eq. (4)].[155]

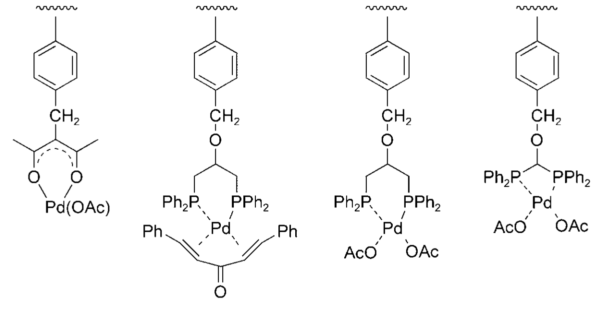
The problems of palladium release resulting in homogeneous catalytic activity was again observed by Schuchardt et al, when they applied organic polymers as new supports for heterogenization (for example, linear poly(vinylpyridines) or 2,2′-dipyridyl-functionalized poly(styrene/divinylbenzene)).[156]

In asymmetric catalysis an efficient catalyst recycling is particular essential, because the costs of ligands often top those of the catalyst metals. Therefore, Keim et al. heterogenized their successful homogeneous catalyst for the asymmetric telomerization of butadiene with β-ketoesters [Eq. (10)].[157] The chiral information results from the chiral organic ligand (2*S*,4*S*)-2-diphenylphosphino-4-diphenylphosphinomethyl pyrrolidine (PPM), which can be heterogenized on silica or polyacrylate. Both heterogenized catalysts lead yields to comparable with those of the homogeneous catalyst. The release of palladium is 5 wt % per recycling run. In spite of the good results, the separation of the highly swellable polymer turned out to be problematic, because the telomeric products adsorb on the organic polymer.



(10)

Benvenuti et al. use a macroporous resin, consisting crosslinked poly(styrene/divinylbenzene), and a Merrifield powdered resin, composed of a chloromethylated crosslinked poly(styrene/divinylbenzene), their aim was to obtain bidentate ligands bound to solid polymeric matrices (Scheme 12).[152] First investigations of **41** show the release of palladium, probably driven by free triphenylphosphine in solution. Therefore a chelating diphosphine ligand was directly bound to the polymeric support (**42**, **43**). Although the diphosphine chelating ligand gives great stability to the polymer-bound metal complexes, the activity and the selectivity towards telomers are undesirably low. This fact could be explained if the metal coordination sphere is sterically hindered, thus preventing the nucleophilic attack of methanol after insertion of two butadiene molecules (see Section 2.1). Only when using **43** as the catalyst and sodium methoxide as a promoter is a much higher turn over frequency of 220 h^{-1} obtained. Hence, this catalyst really works heterogeneously without appreciable release of metal species into the reaction medium. Later Benvenuti et al. developed novel heterogen-



41 **42** **43** **44**

Scheme 12. Palladium complexes anchored to crosslinked styrene/divinylbenzene resins.

ized palladium(II) complexes by anchoring the metal species to bis(diphenylphosphino)methane (DPPM) chelating moieties (**44**).[158]

7. Conclusions

Over 40 years of research on transition-metal catalyzed telomerization have led to various syntheses, catalyst systems, and processes as well as industrial applications and products. Two important examples are the products obtained by the reaction of butadiene with water and methanol, respectively. The reaction products are used as intermediates in polymer technology, octadienol in plasticizer production and methoxyoctadiene to obtain 1-octene as a co-monomer in the production of LLDPE.

Other products, such as telomers of sugars or glycerol, can be used as biodegradable emulsifiers made of renewable materials. Owing to their skin- and eco-friendliness, they are interesting ingredients for the cosmetic and pharmaceutical industry.

Telomers of amines are also useful starting materials for detergent or fabric softener production. Telomers of butadiene with acetic acid or phenol as well as telomers of isoprene with various nucleophiles are useful intermediates in the production of flavors and fragrances. Especially telomers of isoprene may become of importance as a result of their structural similarity to natural terpenes.

Multifunctional products, such as lactones or nonadieonates, which can be easily converted into natural flavors and fragrances are obtained by telomerization in the presence of CO_2 or CO. These are typical examples for the most important advantages of telomerizations: Multifunctional complex products can be formed out of easily accessible starting materials in an atom-economic reaction under mild conditions.

Received: September 18, 2008
Published online: March 3, 2009

---

[1] E. J. Smutny, *J. Am. Chem. Soc.* **1967**, *89*, 6793 – 6794.
[2] S. Takahashi, T. Shibano, N. Hagihara, *Tetrahedron Lett.* **1967**, *8*, 2451 – 2453.
[3] A. Behr in *Aspects Homogeneous Catalysis, Vol. 5* (Ed.: R. Ugo), D. Reidel Publishing, Dordrecht, **1984**, pp. 3 – 73.
[4] R. Benn, P. W. Jolly, T. Joswig, R. Mynott, K. P. Schick, *Z. Naturforsch. B* **1986**, *41*, 680 – 691.
[5] R. Benn, P. W. Jolly, R. Mynott, B. Raspel, G. Schenker, K. P. Schick, G. Schroth, *Organometallics* **1985**, *4*, 1945 – 1953.
[6] A. Döhring, P. W. Jolly, R. Mynott, K. P. Schick, G. Wilke, *Z. Naturforsch. B* **1981**, *36*, 1198 – 1199.
[7] P. W. Jolly, *Angew. Chem.* **1985**, *97*, 279 – 291; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 283 – 295.
[8] P. W. Jolly, R. Mynott, B. Raspel, K. P. Schick, *Organometallics* **1986**, *5*, 473 – 481.
[9] A. Behr, G. von Ilsemann, W. Keim, C. Krüger, Y.-H. Tsay, *Organometallics* **1986**, *5*, 514 – 518.
[10] W. Keim, *Angew. Chem.* **1968**, *80*, 968 – 969; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 879 – 880.
[11] W. Keim in *Transition Metals in Homogeneous Catalysis* (Ed.: G. N. Schrauzer), Marcel Dekker, New York, **1971**.
[12] R. Jackstell, A. Grotevendt, D. Michalik, L. El Firdoussi, M. Beller, *J. Organomet. Chem.* **2007**, *692*, 4737 – 4744.
[13] N. Yoshimura in *Aqueous-Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2004**, chap. 6.9, p. 540.
[14] T. Maeda, Y. Tokitoh, N. Yoshimura (Kuraray Co., Ltd.), EP0296550, **1988**.
[15] K. E. Atkins, W. E. Walker, R. M. Manyik, *Chem. Commun.* **1971**, 330.
[16] E. Monflier, P. Bourdauducq, J.-L. Couturier, J. Kervennal, I. Suisse, A. Mortreux, *Catal. Lett.* **1995**, *34*, 201 – 212.
[17] E. Monflier, P. Bourdauducq, J.-L. Couturier, J. Kervennal, A. Mortreux, *Appl. Catal. A* **1995**, *131*, 167 – 178.
[18] E. Monflier, P. Bourdauducq, J.-L. Couturier, J. Kervennal, A. Mortreux, *J. Mol. Catal. A* **1995**, *97*, 29 – 33.
[19] B. I. Lee, K. H. Lee, J. S. Lee, *J. Mol. Catal. A* **2001**, *166*, 233 – 242.
[20] J. Čermák, M. Kvicalova, V. Blechta, *Collect. Czech. Chem. Commun.* **1997**, *62*, 355 – 363.
[21] J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza, J. Dupont, J. Fischer, A. De Cian, *Organometallics* **1998**, *17*, 815 – 819.
[22] D. Dehn, PhD thesis, Technische Universität Dortmund, **2007**.
[23] A. Tafesh, M. Beller, J. Krause (Hoechst GmbH and Co. KG), WO9808794, **1998**.
[24] M. Röper, W. Bertleff, D. Köffer (BASF AG), EP0330999, **1989**.
[25] B. J. Schaart, H. L. Pelt, G. B. Jacobsen (Dow Chemical Company), US5254782A1, **1993**.
[26] R. Jackstell, A. Frisch, M. Beller, D. Röttger, M. Malaun, B. Bildstein, *J. Mol. Catal. A* **2002**, *185*, 105 – 112.
[27] 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 – 1030.
[28] R. Jackstell, S. Harkal, H. Jiao, A. Spannenberg, C. Borgmann, D. Röttger, F. Nierlich, M. Elliot, S. Niven, K. Cavell, O. Navarro, M. Viciu, S. P. Nolan, M. Beller, *Chem. Eur. J.* **2004**, *10*, 3891 – 3900.
[29] M. Beller, H. Klein, R. Jackstell, D. Röttger (Oxeno), CA2490332A1, **2004**.
[30] D. Röttger, R. Jackstell, H. Klein, M. Beller (Oxeno), US2005240039A1, **2005**.
[31] M. Beller, N. D. Clement, L. Routaboul, A. Grotevendt, R. Jackstell, *Chem. Eur. J.* **2008**, *14*, 7408 – 7420.
[32] R. M. Hanes (Nat Distillers Chem. Corp.), US4642392A1, **1987**.
[33] R. M. Hanes (Nat Distillers Chem. Corp.), US4831183A1, **1989**.

[34] E. Drent, M. R. Eberhard, P. G. Pringle, R. H. van der Made (Shell), US2006084832A1, **2006**.

[35] M. Basato, L. Crociani, F. Benvenuti, A. M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A* **1999**, *145*, 313 – 316.

[36] F. Benvenuti, C. Carlini, M. Marchionna, R. Patrini, A. M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A* **1999**, *140*, 139 – 155.

[37] L. Crociani, G. Bandoli, A. Dolmella, M. Basato, B. Corain, *Eur. J. Inorg. Chem.* **1998**, 1811 – 1820.

[38] B. Estrine, B. Blanco, S. Bouquillon, F. Hénin, M. Moreno-Manas, J. Muzart, C. Pena, R. Pleixats, *Tetrahedron Lett.* **2001**, *42*, 7055 – 7057.

[39] M. Camargo, P. Dani, J. Dupont, R. F. de Souza, M. Pfeffer, I. Tkatchenko, *J. Mol. Catal. A* **1996**, *109*, 127 – 131.

[40] F. Bouachir, P. Grenouillet, D. Neibecker, J. Poirier, I. Tkatchenko, *J. Organomet. Chem.* **1998**, *569*, 203 – 215.

[41] Y. Chauvin, L. Magna, G. P. Niccolai, J.-M. Basset (Celanese GmbH), EP1201634A1, **2002**.

[42] R. C. Bohley, G. B. Jacobsen, H. L. Pelt, B. J. Schaart, M. Schenk, D. A. G. van Oeffelen (Dow Benelux), WO9210450A1, **1992**.

[43] C. L. Edwards (Shell), WO2005019139, **2005**.

[44] D. Röttger, A. Tuchlenski (Oxeno), US2004059170, **2004**.

[45] R. Patrini, M. Lami, M. Marchionna, F. Benvenuti, A. M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A* **1998**, *129*, 179 – 189.

[46] H. Anderson, N. Heldt, *Thermochim. Acta* **1993**, *229*, 235 – 242.

[47] H. Anderson, N. Heldt, K. Heldt, *Chem. Ing. Tech.* **1994**, *66*, 69 – 72.

[48] N. Heldt, K. Heldt, H. Anderson, W. Gaube, *J. Therm. Anal.* **1993**, *40*, 1213 – 1221.

[49] N. Heldt, K. Lühder, W. Gaube, *React. Kinet. Catal. Lett.* **1995**, *54*, 239 – 245.

[50] R. C. Nunes, M. H. Araujo, E. N. dos Santos, *Catal. Commun.* **2007**, *8*, 1798 – 1802.

[51] A. Behr, T. Fischer, M. Grote, D. Schnitzmeier, *Chem. Ing. Tech.* **2002**, *74*, 1586 – 1591.

[52] P. Dani, J. Dupont, A. L. Monteiro, *J. Braz. Chem. Soc.* **1996**, *7*, 15 – 18.

[53] W. Keim, A. Kraus, K. Huthmacher, R. Hahn (Degussa AG), DE 19730546A1, **1999**.

[54] A. Behr, J. Seuster in *Multiphase Homogeneous Catalysis* (Eds.: B. Cornils, H. Olivier-Bourbigou), Wiley-VCH, Weinheim, **2005**, pp. 114 – 122.

[55] A. Behr, M. Urschey, V. A. Brehme, *Green Chem.* **2003**, *5*, 198 – 204.

[56] A. Behr, M. Urschey, *J. Mol. Catal. A* **2003**, *197*, 101 – 113.

[57] A. Behr, M. Urschey, *Adv. Synth. Catal.* **2003**, *345*, 1242 – 1246.

[58] M. Urschey, PhD thesis, Technische Universität Dortmund, **2004**.

[59] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chem.* **2008**, *10*, 13 – 30.

[60] A. Behr, J. Leschinski, C. Awungacha, S. Simic, T. Knoth, *ChemSusChem* **2009**, *2*, 71 – 76.

[61] A. Behr, J. Leschinski, *40. Jahrestreffen Deutscher Katalytiker*, Weimar, **2007**.

[62] R. Palkovits, I. Nieddu, R. J. M. Klein Gebbink, B. M. Weckhuysen, *ChemSusChem* **2008**, *1*, 193 – 196.

[63] A. Bessmertnykh, F. Hénin, J. Muzart, *J. Mol. Catal. A* **2005**, *238*, 199 – 206.

[64] C. Damez, B. Estrine, A. Bessmertnykh, S. Bouquillon, F. Hénin, J. Muzart, *J. Mol. Catal. A* **2006**, *244*, 93 – 98.

[65] B. Estrine, S. Bouquillon, F. Hénin, J. Muzart, *Eur. J. Org. Chem.* **2004**, 2914 – 2922.

[66] B. Estrine, S. Bouquillon, F. Hénin, J. Muzart, *Green Chem.* **2005**, *7*, 219 – 223.

[67] A. Bessmertnykh, F. Hénin, A. Serra-Muns, J. Muzart, H. Baillia, *Carbohydr. Res.* **2006**, *341*, 153 – 159.

[68] V. Desvergnes-Breuil, C. Pinel, P. Gallezot, *Green Chem.* **2001**, *3*, 175 – 177.

[69] I. Pennequin, J. Meyer, I. Suisse, A. Mortreux, *J. Mol. Catal. A* **1997**, *120*, 139 – 142.

[70] K. Hill, B. Gruber, K. J. Weese, *Tetrahedron Lett.* **1994**, *35*, 4541 – 4542.

[71] U. Donzé, C. Pinel, P. Gallezot, P. L. Taylor, *Adv. Synth. Catal.* **2002**, *344*, 906 – 910.

[72] B. Fabry, B. Gruber (Henkel), DE4020973, **1992**.

[73] H.-C. Raths, B. Gruber, D. Ouzounis (Henkel), DE4021478, **1992**.

[74] F. Wangemann (Henkel), DE4114243, **1992**.

[75] B. Gruber, U. Eicken, H. Fischer (Henkel), DE4129527, **1993**.

[76] R. Müller, B. Gruber, F. Wangemann, K. Seidel, D. Hollenberg (Henkel), WO9316156, **1993**.

[77] K. Hill, U. Mahler (Henkel), WO9202284A1, **1992**.

[78] P. Höhlein, J. Meixner, J. Pedain (Bayer), DE4141190, **1993**.

[79] B. Gruber, U. Eicken, N. Stork (Henkel), DE4129528, **1993**.

[80] C. Hadad, C. Damez, S. Bouquillon, B. Estrine, F. Hénin, J. Muzart, I. Pezron, L. Komunjer, *Carbohydr. Res.* **2006**, *341*, 1938 – 1944.

[81] R. Bunte, B. Gruber, J. Tucker (Henkel), DE4021511, **1992**.

[82] K. Hill, S. D. Axt, K. J. Weese (Henkel), US5198598, **1993**.

[83] R. Patrini, M. Marchionna (Snamprogetti SpA), EP0613875A1, **1994**.

[84] I. Pennequin, A. Mortreux, F. Petit, J. Mentech, B. Thiriet (Eridania Beghin-Say), FR2693188, **1994**.

[85] E. J. Smutny (Shell), US 3518318, **1970**.

[86] A. Krotz, F. Vollmüller, G. Stark, M. Beller, *Chem. Commun.* **2001**, 195 – 196.

[87] F. Vollmüller, PhD thesis, Technische Universität München, **1998**.

[88] A. Behr, T. Beckmann in *Processnet Jahrestagung*, Aachen, **2007**.

[89] W. E. Walker, R. M. Manyik, K. E. Atkins, M. L. Farmer, *Tetrahedron Lett.* **1970**, *11*, 3817 – 3820.

[90] D. Rose, H. Lepper, *J. Organomet. Chem.* **1973**, *49*, 473 – 476.

[91] For example, L. H. Slaugh (Shell), US 5030792, **1991**.

[92] E. Drent, W. W. Jager (Shell), EP1671940A1, **2004**.

[93] A. Behr, T. Beckmann, *41. Jahrestreffen Deutscher Katalytiker*, Weimar, **2008**.

[94] A. Behr, T. Beckmann, P. Schwach, *J. Organomet. Chem.* **2008**, *693*, 3097 – 3102.

[95] C. U. Pittman, R. M. Hanes, J. J. Yang, *J. Mol. Catal.* **1982**, *15*, 377 – 381.

[96] V. Brehme, M. Neumann, F. Bauer, D. Röttger (Evonik Degussa GmbH), WO2008/003559, **2008**.

[97] J. Beger, F. Meier, *J. Prakt. Chem.* **1980**, *322*, 69 – 80.

[98] A. M. Lazutkin, A. I. Lazutkina, *React. Kinet. Catal. Lett.* **1978**, *8*, 263 – 268.

[99] D. Rose, *Tetrahedron Lett.* **1972**, *11*, 4197 – 4200.

[100] J. Tsuji, M. Takahashi, *J. Mol. Catal.* **1980**, *10*, 107 – 114.

[101] K. Kaneda, H. Kurosaki, M. Terasawa, T. Imanaka, S. Teranishi, *J. Org. Chem.* **1981**, *46*, 2356 – 2362.

[102] M. L. Chernyshev, V. S. Tkach, T. V. Dmitrieva, G. V. Ratovskii, S. V. Zinchenko, F. K. Shmidt, *React. Kinet. Catal. Lett.* **1992**, *48*, 291 – 294.

[103] M. S. Viciu, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2003**, *22*, 3175 – 3177.

[104] A. Grotevendt, M. Bartolome, D. J. Nielsen, A. Spannenberg, R. Jackstell, K. J. Cavell, L. A. Oro, M. Beller, *Tetrahedron Lett.* **2007**, *48*, 9203 – 9207.

[105] T. Antonsson, A. Langlét, C. Moberg, *J. Organomet. Chem.* **1989**, *363*, 237 – 241.

[106] T. Prinz, W. Keim, B. Drießen-Hölscher, *Angew. Chem.* **1996**, *108*, 1835 – 1836; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1708 – 1710.
[107] T. Prinz, B. Drießen-Hölscher, *Chem. Eur. J.* **1999**, *5*, 2069 – 2076.
[108] B. Drießen-Hölscher in *Multiphase Homogeneous Catalysis* (Ed.: B. Cornils), Wiley-VCH, Weinheim, **2005**, pp. 238 – 244.
[109] H. J. Traenckner, J. Jentsch, T. Prinz, B. Drießen-Hölscher, W. Keim (Bayer AG), DE19808260, **1998**.
[110] G. S. Santos Fonseca, R. F. de Souza, J. Dupont, *Catal. Commun.* **2002**, *3*, 377 – 380.
[111] T. Beckmann, PhD thesis, Technische Universität Dortmund, in preparation.
[112] F. Leca, R. Réau, *J. Catal.* **2006**, *238*, 425 – 429.
[113] S. M. Maddock, M. G. Finn, *Organometallics* **2000**, *19*, 2684 – 2689.
[114] E. A. Petrushkina, L. I. Zakharkin, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1992**, *41*, 1392 – 1394.
[115] E. A. Petrushkina, N. E. Mysova, A. V. Orlinkov, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2232 – 2235.
[116] S. Reyer, PhD thesis, Technische Universität Dortmund, in preparation.
[117] A. Behr, L. Johnen in *Dream Reactions—Synthesis and Processes for Sustainable Chemistry*, Aachen, **2008**.
[118] Y. Sasaki, Y. Inoue, H. Hashimoto, *J. Chem. Soc. Chem. Commun.* **1976**, 605 – 606.
[119] A. Musco, C. Perego, V. Tartiari, *Inorg. Chim. Acta* **1978**, *28*, L147.
[120] P. Braunstein, D. Matt, D. Nobel, *J. Am. Chem. Soc.* **1988**, *110*, 3207 – 3212.
[121] P. Braunstein, D. Matt, D. Nobel, *Chem. Rev.* **1988**, *88*, 747 – 764.
[122] A. Behr, *Carbon dioxide activation by metal complexes*, Wiley-VCH, Weinheim, **1988**.
[123] A. Behr, R. He, K. D. Juszak, C. Krüger, Y. H. Tsay, *Chem. Ber.* **1986**, *119*, 991 – 1015.
[124] K. Buchmüller, N. Dahmen, E. Dinjus, D. Neumann, B. Powietzka, S. Pitter, J. Schön, *Green Chem.* **2003**, *5*, 218 – 223.
[125] N. Holzhey, PhD thesis, Universität Heidelberg, **1999**.
[126] N. Holzhey, S. Pitter, *J. Mol. Catal. A* **1999**, *146*, 25 – 36.
[127] N. Holzhey, S. Pitter, E. Dinjus, *J. Organomet. Chem.* **1997**, *541*, 243 – 248.
[128] E. Dinjus, W. Leitner, *Appl. Organomet. Chem.* **1995**, *9*, 43 – 50.
[129] S. Pitter, E. Dinjus, *J. Mol. Catal. A* **1997**, *125*, 39 – 45.
[130] S. Pitter, E. Dinjus, B. Jung, H. Görls, *Z. Naturforsch. B* **1996**, *51*, 934 – 946.
[131] A. Daniels (ICI), EP0050445, **1982**.
[132] M. Heite, PhD thesis, Technische Universität Dortmund, **1999**.
[133] A. Behr, M. Heite, *Chem. Eng. Technol.* **2000**, *23*, 952 – 955.
[134] A. Behr, M. Heite, *Chem. Ing. Tech.* **2000**, *72*, 58 – 61.
[135] A. Behr, W. Ebbers, *35. Jahrestreffen Deutscher Katalytiker*, Weimar, **2002**.
[136] P. Bahke, PhD thesis, Technische Universität Dortmund, **2005**.
[137] A. Behr, P. Bahke, M. Becker, *Chem. Ing. Tech.* **2004**, *76*, 1828 – 1832.
[138] A. Behr, P. Bahke, B. Klinger, M. Becker, *J. Mol. Catal. A* **2007**, *267*, 149 – 156.
[139] J. Tsuji, H. Yasuda, *J. Organomet. Chem.* **1977**, *131*, 133 – 135.
[140] M. G. Romanelli (Esso Research and Engineering Co.), US3780074, **1973**.
[141] C. Bordenca, W. E. Marsico, *Tetrahedron Lett.* **1967**, *8*, 1541 – 1543.
[142] K. Bittler, N. von Kutepow, D. Neubauer, H. Reis, *Angew. Chem.* **1968**, *80*, 352 – 359; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 329 – 335.
[143] W. E. Billups, W. E. Walker, T. C. Shields, *Chem. Commun.* **1971**, 1067 – 1068.
[144] J. Tsuji, Y. Mori, M. Hara, *Tetrahedron* **1972**, *28*, 3721 – 3725.
[145] J. F. Knifton, *J. Catal.* **1979**, *60*, 27 – 40.
[146] J. F. Knifton (Texaco Development Corp., USA), GB2014136, **1979**.
[147] P. Foley (Celanese Corp., USA), US4416823, **1983**.
[148] J. Kiji, T. Okano, K. Odagiri, N. Ueshima, H. Konishi, *J. Mol. Catal.* **1983**, *18*, 109 – 112.
[149] T. H. Vanderspurt, P. M. Zema (Celanese Corp., USA), US4269781, **1981**.
[150] R. Schöbel, PhD thesis, Technische Universität Dortmund, **2009**.
[151] A. M. Lazutkin, A. I. Lazutkina, Y. I. Yermakov, *React. Kinet. Catal. Lett.* **1978**, *8*, 353 – 357.
[152] F. Benvenuti, C. Carlini, A. M. Raspolli Galletti, G. Sbrana, M. Marchionna, R. Patrini, *J. Mol. Catal. A* **1999**, *137*, 49 – 63.
[153] B. I. Lee, K. H. Lee, J. S. Lee, *J. Mol. Catal. A* **2000**, *156*, 283 – 287.
[154] B. Estrine, R. Soler, C. Damez, S. Bouquillon, F. Hénin, J. Muzart, *Green Chem.* **2003**, *5*, 686 – 689.
[155] B. Estrine, S. Bouquillon, F. Hénin, J. Muzart, *Appl. Organomet. Chem.* **2007**, *21*, 945 – 946.
[156] U. Schuchardt, E. N. dos Santos, F. Santos Dias, *J. Mol. Catal.* **1989**, *55*, 340 – 352.
[157] W. Keim, D. Schwarzer, D. Vogt, *Chem. Ing. Tech.* **1995**, *67*, 903 – 904.
[158] F. Benvenuti, C. Carlini, M. Marchionna, R. Patrini, A. M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal. A* **1999**, *139*, 177 – 187.