Palladium-Catalyzed Reactions for the Synthesis of Fine Chemicals, 14[+]

Control of Chemo- and Regioselectivity in the Palladium-Catalyzed Telomerization of Butadiene with Methanol − Catalysis and Mechanism

Frank Vollmüller,[a] Jochen Krause,*[b] Susanne Klein,[b] Wolfgang Mägerlein,[c] and Matthias Beller*[c]

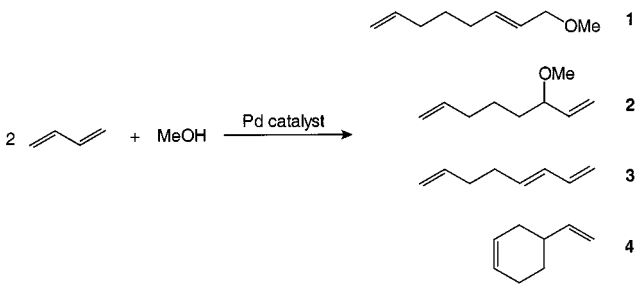
Keywords: Palladium / Butadiene / Telomerization / Homogeneous catalysis

The palladium-catalyzed telomerization reaction of butadiene with methanol has been examined with the aim of controlling the chemoselectivity (telomerization vs. dimerization products) and regioselectivity (linear vs. branched telomerization product) of the reaction. We have shown that the reaction temperature, ligand-to-metal ratio and ratio of substrates exert a large influence on the selectivity of the reaction. Selectivities of up to 97% for the desired linear telomerization product **1** can be achieved below 50 °C by employing both low PPh_3/Pd and butadiene/methanol ratios. Mono(phosphane)palladium(0)–diallyl ether complexes, Ar_3P–Pd[$(CH_2=CHCH_2)_2O$] (**5**), serve as new catalysts for the reaction. In order to gain a mechanistic understanding of the observed selectivity effects, we synthesized the phosphane(octadienyl)palladium(II) complexes **7a** and **9a** as model compounds for key reaction intermediates and examined their stoichiometric reactions with the methoxide nucleophile. Based on our results, we propose an extension of the known telomerization mechanism that accounts for the observed selectivity effects.

Introduction

An important ecological requirement of todays chemical processes is to produce a desired compound with high selectivity whilst, as far as possible, avoiding waste or by-products. Therefore, the possibility of controlling the product selectivity in a chemical reaction is of great interest. This control can be achieved, for example, by employing an appropriate catalyst or by adjusting the crucial reaction parameters.

During the course of our studies with regard to palladium-catalyzed C−C coupling reactions we became interested in the telomerization of butadiene, since this reaction assembles simple starting materials in a 100% atom-efficient manner to give valuable functionalized octadienes. These compounds are useful as intermediates in the total synthesis of several natural products,[2] as well as in industry, as precursors for plasticizer alcohols,[3] solvents, corrosion inhibitors and nonvolatile herbicides.[4] The telomerization reaction is the dimerization of two molecules of a 1,3-diene in the presence of an appropriate nucleophile HX,[5] e.g. alcohols,[6] water,[7] amines,[8] carboxylic acids[9] and others,[10] to give substituted octadienes (1-substituted 2,7-octadiene, 3-substituted 1,7-octadiene). Of these the 1-substituted 2,7-octadiene (*n*-product) is the major isomer formed for most nucleophiles. Due to the fact that they are readily available and cheap,[11] butadiene and methanol are attractive starting materials for this reaction, reacting to yield 1-methoxyocta-2,7-diene (**1**) (Scheme 1). As previous studies have shown,[6j] the major by-products include the 3-substituted octa-1,7-diene **2** (iso product), 1,3,7-octatriene (**3**) (formed by the linear dimerization of butadiene) and, less importantly, 4-vinylcyclohexene (**4**) (formed by the Diels−Alder reaction of two molecules of butadiene).



Scheme 1

Although the mechanism of the palladium-catalyzed telomerization reaction has been carefully examined,[12] de-

[+] Part 13: Ref.[1]

[a] Clariant Deutschland GmbH, Division Feinchemikalien, Industriepark Höchst,
65916 Frankfurt am Main, Germany
Fax: (internat) + 49-(0)69/30517562
E-mail: frank.vollmueller@clariant.com
[b] Clariant Deutschland GmbH, Division Feinchemikalien, Werk Griesheim
Postfach 831251, 65916 Frankfurt am Main, Germany
Fax. (internat) + 49-(0)69/386411
E-mail: jochen.krause@clariant.com
[c] Institut für Organische Katalyseforschung an der Universität Rostock e.V.
Buchbinderstraße 5−6, 18055 Rostock, Germany
Fax: (internat) + 49-(0)381/4669324
E-mail: matthias.beller@ifok.uni-rostock.de

  1434−1948/00/0808−1825 $ 17.50+.50/0

tailed investigations focusing on the control of product selectivity in this process have not yet been carried out. In this paper, we describe the important factors determining the chemo- and regioselectivity, i.e. reaction temperature, ligand-to-metal ratio and butadiene-to-methanol ratio. New mono(phosphane)palladium(0) complexes **5**[13] were successfully employed as catalysts. The observed effects are rationalized mechanistically by a modified reaction mechanism for the butadiene telomerization reaction.

Results and Discussion

The examined telomerization reaction of butadiene with methanol is shown in Scheme 1.[14] Either (diallyl ether)(triphenylphosphane)palladium(0) (**5**)[13] or mixtures of palladium(II) acetate and triphenylphosphane (sometimes in combination with triethylamine) were used as the catalysts (Figure 1).

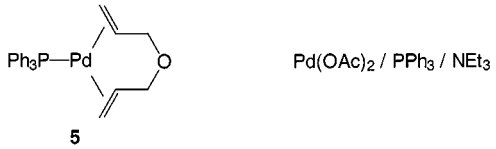


Figure 1

Compound **5** is representative of a new class of palladium(0) complexes in which only *one* phosphane ligand is coordinated to the palladium center. Compound **5** represents a stable analogue of an intermediate in the catalytic cycle of the reaction (vide infra, Schemes 2 and 5) and, as such, is well suited for our investigations, since it does not need to be activated (e.g. by ligand dissociation, reduction, etc.) before entering the catalytic cycle. For reasons of industrial applicability we have also included Pd^{II} precursor complexes in our studies due to the great availability of $Pd(OAc)_2$. It has already been reported that Pd^{II} precursors are rapidly reduced to the catalytically active Pd^0 species if a base, e.g. NEt_3, is present in the reaction mixture.[15] Thus, 100 equivalents NEt_3 (relative to Pd) were added to the runs in which the Pd^{II} precursor complex was used. Initial experiments showed that the content of NEt_3 in the reaction does not influence the chemo- nor the regioselectivity of the telomerization. Therefore, for the selectivity studies it was less important if the applied catalyst precursor was a Pd^0 or a Pd^{II} compound.

Selectivity Studies

The product selectivity of the palladium-catalyzed telomerization is largely influenced by temperature, ratio of starting materials and concentration of the phosphane ligands. Table 1 summarizes the influence of the reaction temperature.

The chemoselectivity, i.e. the discrimination between telomerization products (**1**, **2**) and the linear dimerization product 1,3,7-octatriene (**3**), remains excellent (95%) up to 50 °C (Entries 1−3, Table 1) but drops to 77% at 90 °C (Entry 4; Table 1). Thus, the high catalytic activity at elevated temperatures [turnover frequency (TOF) = 21000 h^{-1}: Entry 4, Table 1] is at the expense of the chemoselectivity. Above 100 °C, the Diels−Alder reaction of butadiene to yield 4-vinylcyclohexene becomes increasingly significant. On the other hand, the regioselectivity, i.e. the discrimination between both telomers **1** and **2**, remains high (≥ 95%) throughout the whole temperature range examined. Obviously, the side reaction leading to the undesired octatriene **3** becomes more important at temperatures above 50 °C, whereas the side reaction leading to the undesired iso telomer **2** is influenced by temperature to a much lesser extent. For palladium-catalyzed reactions in general, the ligand-to-metal ratio is one of the most critical reaction parameters. Typically, the variation of the ligand-to-palladium ratio influences the stability and the activity of the palladium catalyst but has a less pronounced effect on the reaction selectivity. Interestingly, in the case of the butadiene telomerization reaction the P/Pd ratio does not only influence the catalyst stability and activity but also dramatically affects the regioselectivity of the reaction. This effect was observed for both catalyst systems shown in Figure 1. The results of the catalytic runs with 1, 2, 3, 10 and 50 equivalents of phosphane (with respect to palladium) are shown in Table 2.

Firstly, the influence of the ligand-to-metal ratio on the selectivity was studied at −10 °C. The telomerization reaction was carried out using the palladium(0) complex **5** without any additional triphenylphosphane (P/Pd = 1:1: Entry 1, Table 2), as well as in the presence of 1 equiv. of triphenylphosphane (P/Pd = 2:1: Entry 2, Table 2). In both cases

Table 1. Influence of the reaction temperature on the product selectivity

Entry	Ratio butadiene/ methanol	Catalyst	Catalyst concentration [mol-%]	Temp. [°C]	Reaction time [h]	Conversion [%]	TON **1** + **2** + **3**	TOF [h^{-1}]	Yield **1** + **2** [%]	Yield **3** [%]	Chemoselectivity (**1** + **2**) [%]	Regioselectivity [%] (*n*/iso)
1	2:1	**5**	7×10^{-2}	−10	6	64	914	152	63	1	98	97.3 (36:1)
2	1:2	**5**	2.5×10^{-2}	30	2.5	36	1376	556	34	0.4	95	97.3 (36:1)
3	2:1	**5**	4×10^{-3}	50	2	27	6750	3375	26	1	96	95.8 (23:1)
4	2:1	**5**	1×10^{-3}	90	0.5	11	10500	21000	8.5	2	77	95.0 (19:1)

Table 2. Variation of the palladium to phosphane ratio

Entry	Ratio butadiene/ methanol	Catalyst	Catalyst concentration [mol-%]	Temp. [°C]	Reaction time [h]	Additives	Conversion [%]	TON **1** + **2** + **3**	Yield **1** + **2** [%]	Yield **3** [%]	Chemoselectivity (**1** + **2**) [%]	Regioselectivity [%] (*n*/iso)
1	2:1	**5**	7×10^{-2}	−10	6	–	64	914	63	1	98	97.3 (36:1)
2	2:1	**5**:1 PPh_3	5×10^{-2}	−10	6	–	29	560	28	0.3	97	92.3 (12:1)
3	1:2	**5**	4×10^{-3}	50	2	–	35	8500	34	0	97	97.0 (32:1)
4	1:2	$Pd(OAc)_2$ 3 PPh_3	1×10^{-2}	50	2.5	100 equiv. NEt_3	63	6200	61	1	97	96.6 (28:1)
5	1:2	$Pd(OAc)_2$ 3 PPh_3	1.8×10^{-3}	90	2.5	100 equiv. NEt_3	58	30280	49.5	5	85	95.0 (19:1)
6	1:2	$Pd(OAc)_2$ 10 PPh_3	1×10^{-3}	50	16	100 equiv. NEt_3	23	23000	22	1	> 99	94.1 (16:1)
7	1:2	$Pd(OAc)_2$ 10 PPh_3	1.8×10^{-3}	90	2.5	100 equiv. NEt_3	73	38890	62	8	85	93.3 (14:1)
8	2:1	$Pd(OAc)_2$ 50 PPh_3	5×10^{-4}	50	16	100 equiv. NEt_3	14	28000	13	< 1	> 99	87.5 (7:1)
9	2:1	$Pd(OAc)_2$ 50 PPh_3	5×10^{-4}	90	16	100 equiv. NEt_3	40	70000	30	5	75	85.7 (6:1)

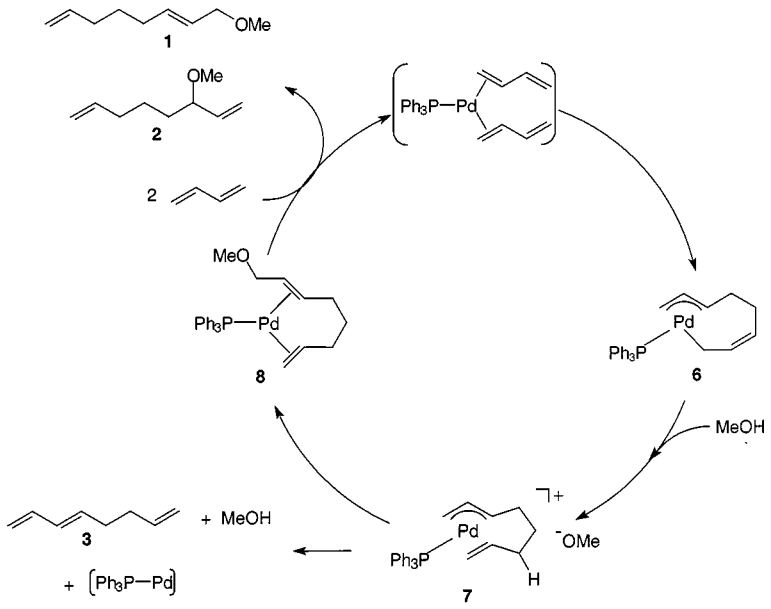
the chemoselectivity towards the telomerization products **1** and **2** was ≥ 97%; however, the *n*/iso ratio changed dramatically. With a P/Pd ratio of 1 the linear isomer **1** was produced in a 36:1 ratio relative to the branched isomer **2**. With a P/Pd ratio of 2 the ratio of **1** to **2** decreased to 12:1. Telomerization reactions using palladium(II) as the pre-catalyst do not yield any telomerization products at −10 °C. At 50 °C, in the presence of the palladium(0) complex **5** (i.e. P/Pd = 1: Entry 3, Table 2), **1** and **2** were still produced with both a high chemoselectivity of 97% and a high *n*/iso ratio of 32:1. On changing to $Pd(OAc)_2$ with 3 equiv. of triphenylphosphane (Entry 4, Table 2), the *n*/iso ratio drops slightly to 28:1, while the chemoselectivity remains excellent (97%). A further increase in the amount of triphenylphosphane at this temperature reduces the regioselectivity, thus the *n*/iso ratio decreases to 16:1 (P/Pd = 10:1: Entry 6; Table 2) and to 7:1 (P/Pd = 50:1: Entry 8, Table 2). However, the chemoselectivity (97−99%) is not affected to any significant extent by the change in the P/Pd ratio. When the telomerization reaction was carried out at 90 °C, both the chemo- and the regioselectivity were influenced by the P/Pd ratio. In the presence of 3 equiv. and 10 equiv. of triphenylphosphane (Entries 5 and 7, Table 2) the chemoselectivity decreases to 85%, and to 75% in the presence of 50 equiv. of the ligand (Entry 9, Table 2). The main side-product observed at 90 °C is 1,3,7-octatriene (**3**). In addition, the *n*/iso selectivity decreases with an increase in the reaction temperature and with an increasing P/Pd ratio. Hence, at 90 °C the linear-to-branched ratio decreases from 19:1 (3 equiv. PPh_3: Entry 5, Table 2) to 14:1 (10 equiv. PPh_3: Entry 7, Table 2). With 50 equiv. of triphenylphosphane the *n*/iso ratio was 6:1 (Entry 9, Table 2), similar to the run at 50 °C (Entry 8; Table 2).

In general, the ratio of telomerization products to dimerization products (chemoselectivity) decreases above a certain temperature (50 °C) and is not really affected by the P/Pd ratio. On the other hand, the regioselectivity is predominantly influenced by the amount of ligand present! The best regioselectivity using triphenylphosphane as the ligand is obtained with a ligand-to-palladium ratio of 1:1 below 50 °C (*n*/iso > 32:1; Entries 1 and 3, Table 2) while a *n*/iso ratio below 6:1 (Entries 8 and 9, Table 2) seems to be the borderline selectivity at high P/Pd ratios.

It is interesting to note that the established reaction mechanism ("Jolly mechanism") for the telomerization of butadiene and methanol (Scheme 2) does not explain the observed changes in regioselectivity.[12e]

It is proposed that in the presence of palladium(0) species two molecules of butadiene couple to form the $PPh_3-Pd-(\eta^1,\eta^3$-octadiendiyl) complex **6**. Protonation by methanol at the C-6 atom of the C_8 chain leads to the $PPh_3-Pd-(\eta^2,\eta^3-C_8H_{13})$ species **7**. In the following step the methoxide ion adds to either allylic terminus C-1 or C-3 of the C_8 chain resulting in the formation of the telomers **1** (via **8**) or **2**, respectively. The formation of 1,3,7-octatriene (**3**) occurs as a side reaction by hydrogen abstraction (C-4) from **7**.

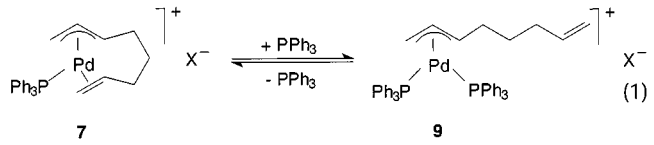
The regioselectivity-determining step of the process is the nucleophilic attack of methanol or methoxide ion on the (π-allyl)mono(phosphane)palladium complex **7**. The nucleophilic attack at the C-1 atom is favored for steric reasons, while the attack at the C-3 atom is electronically favored.[16] Moreover, the linear telomer is the thermodynamically more stable product due to the internal double bond, whereas the branched isomer with the terminal double bond is less stable. However, our control experiments with various mixtures of **1** and **2** reveal that the telomerization reaction does not proceed under thermodynamic control at the described reaction conditions, since product formation is not reversible. We propose that the major reason for the selective formation of the linear telomer **1** is the energetically favored formation of a trigonal planar (1,6-diene)palladium complex [LPd(1,6-diene)]. The branched telomer has a 1,7-diene structure which would give rise to a (1,7-diene)-palladium complex. As demonstrated by us, the stability of trigonal planar (1,6-diene)palladium complexes [LPd(1,6-



Scheme 2

diene)] is much higher than those with a 1,7-diene ligand.[13a,13c]

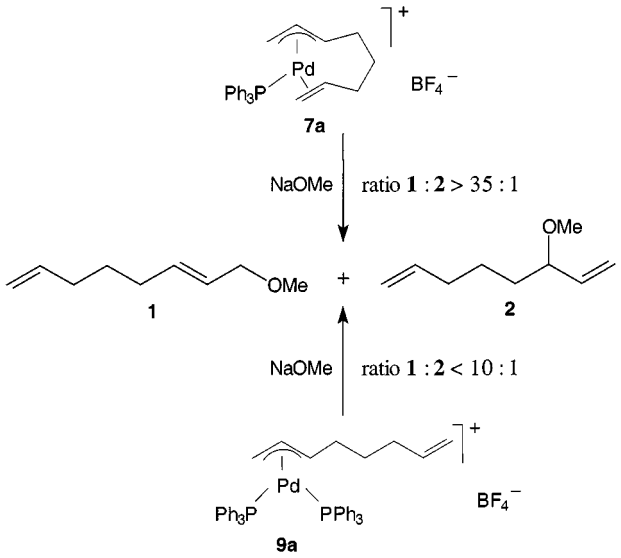
Due to the large influence of the P/Pd ratio on the regioselectivity, we postulate that (π-allyl)bis(phosphane)palladium complexes of type **9** (X = MeO^-) are involved as additional intermediates in the catalytic cycle [Equation (1)].



In complex **9**, nucleophilic attack at the C-1 allylic terminus does not give rise to an energetically favored chelating 1,6-diene coordination of the C_8 chain since coordination of both C−C double bonds is not possible at the P_2Pd^0 moiety. Hence, the greater preference for the linear telomer is less pronounced when compared with **7**. In an attempt to prove this hypothesis, we prepared the (octadienyl)palladium complex **7a** (X = BF_4^-)[12a,17] and reacted it with triphenylphosphane to obtain **9a** (X = BF_4^-). We then investigated the reactions of both **7a** and **9a** with sodium methoxide.

Proceeding from our observation that (diallyl ether)palladium complexes **5** catalyze the telomerization reaction even at low temperatures, we treated **5** with an excess of butadiene at −20 °C and obtained **6** in a quantitative yield.[17] Addition of tetrafluoroboric acid or tetrakis[3,5-bis(trifluoromethyl)phenyl]boric acid[18] in diethyl ether produced the respective cationic complexes of type **7**. The compound with the latter anion has the advantage of a high solubility in organic solvents and is therefore especially suitable for further investigations. On treatment with two equivalents of triphenylphosphane in THF, followed by the addition of pentane, the bis(phosphane)palladium complex **9a** was isolated in a quantitative yield. When excess phosphane was used, the nucleophilic attack of triphenylphosphane on the π-allyl group occurred with concomitant precipitation of tetrakis(triphenylphosphane)palladium.

In order to compare the regioselectivity of the nucleophilic attack of the methoxide anion on **7a** (X = BF_4^-) and **9a** (X = BF_4^-), each complex was treated with a threefold excess of sodium methoxide in THF/methanol (Scheme 3).



Scheme 3

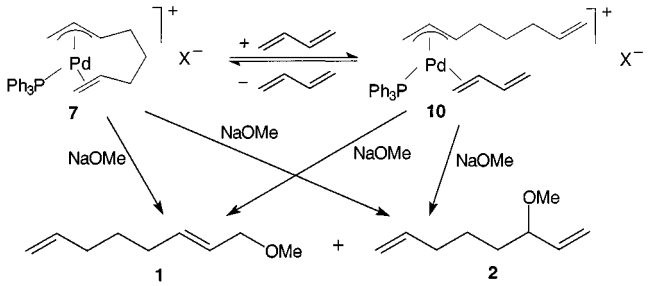
In the case of **7a**, the mixture turned black after a few minutes at room temperature due to the precipitation of palladium metal. GC analysis of the product mixture showed that products **1** and **2** were formed in a ratio > 35:1. The reaction of **9a** with sodium methoxide required slight heating (30 °C) to complete the reaction. GC analysis indicated a ratio of 1:2 < 10:1. Hence, attack of the meth-

Table 3. Variation of the ratio of butadiene to methanol

Entry	Ratio butadiene/ methanol	Catalyst	Catalyst concentration [mol-%]	Temp. [°C]	Reaction time [h]	Conversion [%]	TON **1** + **2** + **3** [%]	Yield **1** + **2** [%]	Yield **3** [%]	Chemoselectivity (**1** + **2**) [%]	Regioselectivity [%] (*n*/iso)
1	2:1	$Pd(OAc)_2$ 3 PPh_3	2×10^{-3}	50	16	43	21500	41	2	95	90.0 (9:1)
2	2:1	$Pd(OAc)_2$ 3 PPh_3	5×10^{-4}	90	16	27	48000	18	6	75	93.8 (15:1)
3	2:1	$Pd(OAc)_2$ 10 PPh_3	2×10^{-3}	50	16	34	17000	33	1	97	87.5 (7:1)
4	2:1	$Pd(OAc)_2$ 10 PPh_3	5×10^{-4}	90	16	35	70000	23	12	66	92.9 (13:1)
5	1:6	$Pd(OAc)_2$ 3 PPh_3	1×10^{-3}	90	16	43	39000	36	3	84	95.5 (21:1)

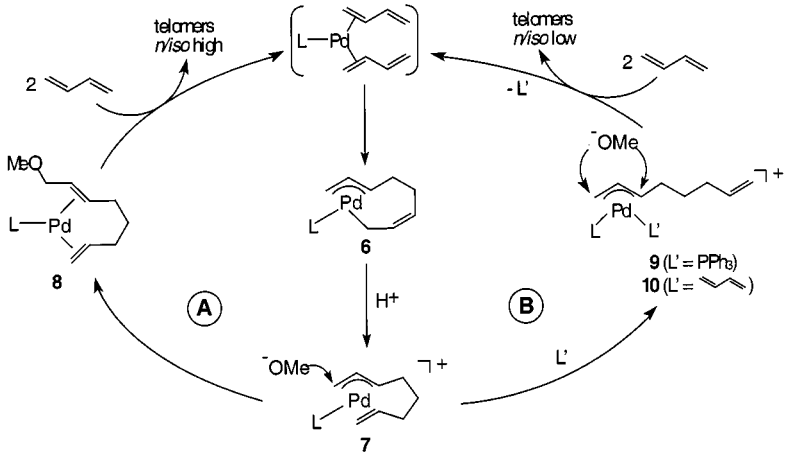
oxide ion on the C-1 allylic terminus in **9a** is less favored than in **7a**, but it is still preferred relative to the C-3 allylic terminus − probably for steric reasons.[16] From these studies it can be concluded that an excess of triphenylphosphane in the telomerization reaction mixture leads to the formation of allylbis(phosphane)palladium complexes of type **9**, which are responsible for a lower *n*/iso ratio of the telomerization products.

Additional support for our selectivity model comes from the fact that the concentration of butadiene also effects the regioselectivity of the attack of methanol on the (allyl)palladium complex. In general, experiments were carried out with a butadiene-to-methanol ratio of 1:2. Apart from this mixture, reactions with a stoichiometric ratio of starting materials and either a large excess of butadiene or methanol were studied. The results are summarized in Table 3.



Scheme 4

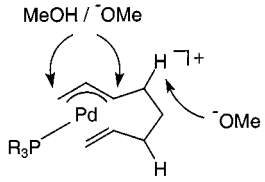
Indeed, we observed that variation in the ratio of starting materials significantly influences the regioselectivity. With increasing concentration of butadiene the yield of the linear telomer **1** decreases (compare Table 2 and 3). More specifically, at 50 °C with a stoichiometric butadiene to methanol ratio, the *n*/iso selectivity is only 9:1 (3 equiv. PPh_3: Entry 1, Table 3) and 7:1 (10 equiv. PPh_3: Entry 3, Table 3), respectively. In contrast, the *n*/iso selectivity totals 28:1 (3 equiv. PPh_3: Entry 4, Table 2) and 16:1 (10 equiv. PPh_3: Entry 6, Table 2) using a reaction mixture that contains a butadiene-to-methanol ratio of 1:2. The same trend holds true at a reaction temperature of 90 °C. In addition, it is shown that employing an excess of methanol, larger than 2:1, has only a small additional positive influence on the regioselectivity (compare Entry 5, Table 2 and Entry 5, Table 3). The influence of the butadiene concentration on the regioselectivity of the telomerization reaction was also observed by Beger et al.,[6b] but has not yet been explained. We suggest that the decrease in regioselectivity with increasing butadiene concentration is due to the loss of the coordination of the internal olefin in **7**. As shown in Scheme 4, the formation of a new intermediate **10** is proposed in the presence of excess butadiene. As stated before, the regioselectivity of the nucleophilic attack on **10** is no longer deter-



Scheme 5

mined by the formation of the favorable complex **8** with a chelating 1,6-diene ligand. Thus, an excess of butadiene has an analogous effect as an excess of phosphane.

The ratio of butadiene to methanol also influences the chemoselectivity of the reaction. Up to 12% of 1,3,7-octatriene (**3**) is produced when stoichiometric amounts of butadiene and methanol are combined at 90 °C (3 equiv. PPh_3: Entry 2; 10 equiv. PPh_3: Entry 4, Table 3). The chemoselectivity is much better at higher methanol concentrations (Entry 5, Table 2 and Entry 5, Table 3). This significant increase in **3** makes it likely that the telomers **1** and **2** result not only from an attack of the corresponding methoxide ion which is produced upon protonation of **6**, but also by the intermolecular reaction of methanol with **7**. While methanol is believed to react only as a nucleophile yielding the telomers, the methoxide anion can react either as a nucleophile or as a base to yield 1,3,7-octatriene (Figure 2). As a result the formation of 1,3,7-octatriene becomes more likely at lower methanol concentrations.



7

Figure 2

Conclusions

In this paper we described a detailed study of the palladium-catalyzed telomerization of butadiene with methanol concerning the control of chemo- and regioselectivity. The selective formation of the linear telomer 1-methoxyocta-2,7-diene (**1**) is influenced by the reaction temperature, the ligand-to-metal ratio and the stoichiometry of the starting materials. By careful optimization of these parameters, *n*/iso selectivities > 35:1 are realized at a low P/Pd ratio of 1:1 and high methanol-to-butadiene ratios in the absence of other coordinating species (regioselectivity up to 97%). *A second phosphane ligand bound to the palladium center dramatically reduces the regioselectivity for **1***. With regard to chemoselectivity, the best results are obtained at low temperatures and high methanol-to-butadiene ratios (chemoselectivity up to 98%). In contrast to the regioselectivity, the chemoselectivity does not depend significantly on the P/Pd ratio.

All our results from the catalysis tests are in general agreement with the previously described mechanism proposed by Jolly. However, in order to explain the observed influences of the P/Pd ratio and the butadiene/Pd ratio on the selectivity we propose an extended mechanistic outline for telomerizations which contains two different reaction pathways (Scheme 5): pathway A going through **7** and **8** (with an energetically favored 1,6-diene C_8-ligand structure) leading to a high *n*/iso selectivity, and pathway B with **9** and **10** as intermediates which react with a lower *n*/iso selectivity as compared with **7**.

A comparison of the reactivity of the isolated complexes **7a** and **9a** with methoxide shows unequivocally that the main principle which governs the *n*/iso selectivity is the internal coordination of the olefinic side-chain. *These results appear to be of general relevance to telomerization reactions with other nucleophiles,* e.g. *this explains why the telomerization of butadiene with acetic acid yields comparably low n/iso ratios.* Thus, it is foreseeable that telomerizations with other oxygen nucleophiles or amines may be controlled by applying the same set of parameters, which we have presented here.

Another result of our work is the discovery that (diallyl ether)mono(phosphane)palladium complexes **5** react with butadiene below 0 °C to give complexes **6**. This allows extremely easy access to the catalytic intermediates of the butadiene telomerization reaction. Furthermore, (diallyl ether)mono(phosphane)palladium complexes are also efficient catalysts for the reaction of butadiene and methanol even at −10 °C. It is likely that these Pd^0 complexes will find use in other catalytic reactions.

Acknowledgments

This work has been performed at the TU München and the former Central Research of Hoechst AG. We thank Prof. Dr. K. Kühlein for his continuing support and Drs. K.-J. Haack, H. Geissler, S. Bogdanovic, R. Fischer, G. Stark and M. Hateley for valuable discussions.

[1] A. Zapf, M. Beller, *Chem. Eur. J.*, in press.

[2] [2a] J. Tsuji, H. Yasuda, T. Mandai, *J. Org. Chem.* **1978**, *43*, 3606. – [2b] J. Tsuji, Y. Kobayashi, T. Takahasi, *Tetrahedron Lett.* **1980**, *21*, 483.

[3] N. Yoshimura, M. Tamura (Kuraray Co. Ltd.), US 4.356.333, **1981**; *Chem. Abstr.* **1982**, *96*, 103630s.

[4] J. Falbe, H. Bahrmann, W. Lipps, D. Mayer, in: *Ullmann's Encyclopedia of Industrial Chemistry*, vol. A1 (Eds.: W. Gerhartz, Y. S. Yamamoto, F. T. Campbell, R. Pfefferkorn, J. F. Rounsaville), VCH, Weinheim, **1985**, p. 279.

[5] For reviews on telomerization reactions see: [5a] W. Keim, A. Behr, M. Röper, in: *Comprehensive Organometallic Chemistry*, vol. 8 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**, p. 372. – [5b] A. Behr, in: *Aspects of Homogeneous Catalysis*, vol. 5 (Ed.: R. Ugo), D. Reidel Publishing Company, Dordrecht, Boston, Lancaster, **1984**, p. 3. – [5c] R. F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, London, **1985**. – [5d] J. M. Takacs, in: *Comprehensive Organometallic Chemistry II*, vol. 12 (Eds: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**, p. 785. – [5e] J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, John Wiley & Sons, Chichester, **1995**, p. 422. – [5f] N. Yoshimura, in: *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 1 (Eds. B. Cornils, W. A. Herrmann) VCH, Weinheim, **1996**, p. 351.

[6] [6a] S. Takahashi, T. Shibano, N. Hagihara, *Tetrahedron Lett.* **1967**, 2451. – [6b] J. Beger, H. Reichel, *J. Prakt. Chem.* **1973**, *315*, 1067. – [6c] J. Beger, C. Duschek, H. Füllbier, W. Gaube, *J. Prakt. Chem.* **1974**, *316*, 26. – [6d] D. Commereuc, Y. Chauvin, *Bull. Soc. Chim. Fr.* **1974**, 652. – [6e] M. Perree-Fauvet, Y. Chauvin, *Tetrahedron Lett.* **1975**, 4559. – [6f] P. Grenouillet, D. Neibecker, J. Poirier, I. Tkatchenko, *Angew. Chem.* **1982**, *94*, 796; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 767. – [6g] R. M. Hanes (National Distillers and Chemical Corporation), US 4.642.392, **1987**; *Chem. Abstr.* **1987**, *107*, 133904x. – [6h] R.

M. Hanes (National Distillers and Chemical Corporation), US 4.831.183, **1989**; *Chem. Abstr.* **1987**, *107*, 133904x. – [6i] G. B. Jacobsen, H. L. Pelt, B. J. Schaart (Dow Chemical Benelux), WO 91 / 09822, **1989**; *Chem. Abstr.* **1991**, *115*, 158514y. – [6j] R. Patrini, M. Lami, M. Marchionna, F. Benvenuti, A. M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal.* **1998**, *129*, 179. – [6k] F. Benvenuti, C. Carlini, M. Marchionna, R. Patrini, A. M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal.* **1999**, *140*, 139. – [6l] M. Basato, L. Crociani, F. Benvenuti, A. M. Raspolli Galletti, G. Sbrana, *J. Mol. Catal.* **1999**, *145*, 313.

[7] [7a] K. E. Atkins, W. E. Walker, R. M. Manyik, *J. Chem. Soc., Chem. Commun*. **1971**, 330. – [7b] T. Maeda, Y. Tokitoh, N. Yoshimura (Kuraray Co. Ltd.), EP 296.550, **1987**; *Chem. Abstr.* **1989**, *110*, 173469c. – [7c] Y. Tokitoh, N. Yoshimura (Kuraray Co. Ltd.), EP 287.066, **1988**; *Chem. Abstr.* **1989**, *110*, 78070g. – [7d] K. Wada, K. Sato, Y. Kasori, Y. Misu (Mitsubishi Kasei Corp.), EP 361.304, **1989**; *Chem. Abstr.* **1990**, *113*, 131562j. – [7e] M. Röper, W. Bertleff, D. Köffer (BASF AG), DE 3.806.305, **1989**; *Chem. Abstr.* **1990**, *112*, 98016p. – [7f] A. Thome, W. Bertleff (BASF AG), US 5.043.487, **1990**; *Chem. Abstr.* **1991**, *114*, 121472m. – [7g] T. Maeda, Y. Tokitoh, N. Yoshimura (Kuraray Co. Ltd.), US 5.100.854, **1990**; *Chem. Abstr.* **1989**, *110*, 173469c. – [7h] Y. Tokitoh, T. Higashi, K. Hino, M. Murasawa, N. Yoshimura (Kuraray Co. Ltd.), EP 436.226, **1990**; *Chem. Abstr.* **1991**, *115*, 158508z. – [7i] D. L. Packett (Union Carbide Corp.), US 5.169.981, **1991**; *Chem. Abstr.* **1993**, *118*, 191171u. – [7j] C. Miyazawa, T. Mori, H. Kameo, S. Isogai (Mitsubishi Kasei Corp.), EP 605.735, **1993**; *Chem. Abstr.* **1994**, *120*, 133838x. – [7k] E. Monflier, P. Bourdauducq, J.-L. Courturier (Elf Atochem S. A.), US 5.345.007, **1993**; *Chem. Abstr.* **1994**, *121*, 179094a. – [7l] J. R. Livingston (Exxon Chemical Patents Inc.), US 5.302.750, **1993**; *Chem. Abstr.* **1994**, *121*, 86253m. – [7m] T. Mori, H. Kameo, S. Isogai, S. Saita (Mitsubishi Chemical Cap.), US 5.583.271, **1995**; *Chem. Abstr.* **1996**, *125*, 142108q. – [7n] E. Monflier, P. Bourdauducq, J. L. Couturier, J. Kervennal, A. Mortreux, *Appl. Catal.* **1995**, *131*, 167. – [7o] E. Monflier, P. Bourdauducq, J. L. Couturier, J. Kervennal, I. Suisse, A. Mortreux, *Catal. Lett.* **1995**, *34*, 201. – [7p] E. Monflier, P. Bourdauducq, J. L. Couturier, J. Kervennal, A. Mortreux, *J. Mol. Catal.* **1995**, *97*, 29.

[8] For aliphatic amines see: [8a] S. Takahashi, T. Shibano, N. Hagihara, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 454. – [8b] J. Beger, F. Meier, *J. Prakt. Chem.* **1980**, *322*, 69. – [8c] U. M. Dzhemilev, G. A. Tolstnikov, A. G. Telin, M. Y. Dolomatov, E. G. Galkin, G. A. Tolstnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 163; *Chem. Abstr.* **1980**, *92*, 197776m. – [8d] C. Moberg, *Tetrahedron Lett.* **1981**, *22*, 4827. – [8e] T. Antonsson, A. Langlet, C. Moberg, *J. Organomet. Chem.* **1989**, *363*, 237. – For anilines see: [8f] K. Takahashi, A. Miyake, G. Hata, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1183. – For ammonia see: [8g] J. Tsuji, M. Takahashi, *J. Mol. Catal.* **1981**, *10*, 107. – [8h] T. Prinz, W. Keim, B. Drießen-Hölscher, *Angew. Chem.* **1996**, *108*, 1835; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1708. – For amino alcohols see: [8i] A. Groult, A. Guy, *Tetrahedron* **1983**, *39*, 1543. For amino acids see: [8j] U. M. Dzhemilev, R. N. Fakhretdinov, A. G. Telin, *Zh. Org. Khim.* **1986**, *22*, 1610; *Chem. Abstr.* **1987**, *107*, 154706z. – For hydrazines see: [8k] A. G. Telin, R. N. Fakhretdinov, U. M. Dzhemilev, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2474. – For hydroxylamines see: [8l] R. N. Fakhretdinov, A. G. Telin, U. M. Dzhemilev, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 2254. – For phthalimides see: [8m] Y. Inoue, M. Taguchi, M. Toyofuku, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3021. – [8n] M. I. Zakharkin, V. V. Guseva, D. D. Sulaimankulova, E. A. Petrushkina, *Zh. Org. Khim.* **1987**, *23*, 1654. – For formamides see: [8o] Y. Inoue, M. Taguchi, M. Toyofuku, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3021.

[9] Acetic acid: [9a] W. E. Walker, R. M. Manyik, K. E. Atkins, M. L. Farmer, *Tetrahedron Lett.* **1970**, 3817. – [9b] D. Rose, H. Lepper, *J. Organomet. Chem.* **1973**, *49*, 473. – Phthalic acid: [9c] R. Fletcher (British Petroleum Company Ltd.), GB 1.505.317, **1976**; *Chem. Abstr.* **1978**, *89*, 90137q. – [9d]W. Keim, A. Durocher, P. Voncken, *Erdöl, Kohle, Erdgas, Petrochem. Brennst.-Chem.* **1976**, *29*, 31. –

[10] For silanols see: [10a] N. Hagihara, S. Takahashi, T. Shibano (Jpn. Pat. 7.700.006), **1977**; *Chem. Abstr.* **1977**, *86*, 189198k. – [10b] M. Capka, P. Svoboda, J. Hetflejs, *Coll. Czech. Chem. Commun.* **1973**, *38*, 1242. – For nitroalkanes see: [10c] T. Mitsuyasu, M. Hara, J. Tsuji, *J. Chem. Soc., Chem. Commun.* **1971**, 345. – [10d] T. Mitsuyasu, J. Tsuji, *Tetrahedron* **1974**, *30*, 831. – [10e] W. Keim, A. Köhnes, T. Röthel, D. Enders, *J. Organomet. Chem.* **1990**, *382*, 295. – For 1,3-dicarbonyl compounds see: [10f] W. Keim, D. Schwarzer, D. Vogt, *Chem.-Ing.-Tech.* **1995**, *67*, 903.

[11] The current industrial price for butadiene is in the range of 0.55−0.65 DM/kg; mixtures of butadiene with other C_4 olefins are even cheaper.

[12] [12a] R. Benn, P. W. Jolly, R. Mynott, B. Raspel, G. Schenker, K.-P. Schick, G. Schroth, *Organometallics* **1985**, *4*, 1945. – [12b] R. Benn, P. W. Jolly, T. Joswig, R. Mynott, K.-P. Schick, *Z. Naturforsch.* **1986**, *41b*, 680. – [12c] A. Döhring, P. W. Jolly, R. Mynott, K.-P. Schick, G. Wilke, *Z. Naturforsch.* **1981**, *36b*, 1198. – [12d] P. W. Jolly, R. Mynott, B. Raspel, K.-P. Schick, *Organometallics* **1986**, *5*, 473. – [12e] P. W. Jolly, *Angew. Chem.* **1985**, *97*, 279; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 283. – [12f] A. Behr, G. v. Ilsemann, W. Keim, C. Krüger, Y.-H. Tsay, *Organometallics* **1986**, *5*, 514.

[13] [13a] J. Krause, Dissertation, Düsseldorf, **1993**. – [13b] J. Krause, K.-J. Haack, G. Cestaric, R. Goddard, K.-R. Pörschke, *Chem. Commun.* **1998**, 1291. – [13c] J. Krause, G. Cestaric, K.-J. Haack, K. Seevogel, W. Storm, K.-R. Pörschke, *J. Am. Chem. Soc.* **1999**, *121*, 9807.

[14] 37 mg (0.14 mmol) of triphenylphosphane and 11 mg (0.05 mmol) of palladium(II) acetate were dissolved in 56 g (1.75 mol) of methanol under argon. The mixture was transferred into a cooled (dry ice) autoclave (Parr model 4561). Subsequently, 54 g (1.00 mol) of butadiene was condensed into the autoclave and the vessel was heated to the reaction temperature. After the reaction was complete, the autoclave was cooled down and the remaining butadiene was recondensed. The conversion was determined by the mass difference of butadiene. The yields of telomerization products were determined by GC (with dodecane as an internal standard) using an HP 6869A gas chromatograph. In order to isolate the octadienyl ethers, the reaction mixture was distilled in vacuo.

[15] R. McCrindle, G. Ferguson, G. J. Arsenault, A. J. McAlees, D. K. Stephenson, *J. Chem. Res. Synop.* **1984**, 360.

[16] [16a] B. Åkermark, S. Hansson, B. Krakenberger, A. Vitagliano, K. Zetterberg, *Organometallics* **1984**, *3*, 679.– [16b] B. Åkermark, A. Vitagliano, *Organometallics* **1985**, *4*, 1275.– [16c] B. Åkermark, K. Zetterberg, S. Hansson, B. Krakenberger, A. Vitagliano, *J. Organomet. Chem.* **1987**, *335*, 133.

[17] **{(1,2,3,7,8-η)-2,7-Octadienyl}(triphenylphosphane)palladium(II) Tetrafluoroborate (7a), {(1,2,3-η)-2,7-Octadienyl}bis(triphenylphosphane)palladium(II) Tetrafluoroborate (9a):** $[Pd(\eta^2,\eta^2\text{-}C_6H_{10}O)(PPh_3)]$ (**5**) (233 mg, 0.50 mmol) was suspended in 8 mL (96 mmol) of butadiene at −78 °C. After warming up to −20 °C, the yellow mixture was stirred for 1 h. Butadiene was removed in vacuo and the remaining light yellow solid was washed with two 5-mL portions of cold pentane. The obtained analytically pure (η^1,η^3-octadienediyl)palladium complex **6** was suspended in 8 mL of diethyl ether at −78 °C. A stoichiometric amount of HBF_4 (68 μL, 0.50 mmol of a 54% solution in diethyl ether) was added to yield a clear yellow solution. After warming to −20 °C and removal of the solvent in vacuo, **7a** was obtained as a yellow powder in a quantitative yield. Complex **9a** was synthesized by slowly adding PPh_3 (52 mg, 0.20 mmol), dissolved in 3 mL of THF, to a solution of **7a** (56 mg, 0.10 mmol) in 3 mL of THF at −60 °C. After stirring the yellow solution for 1 h at −20 °C, pentane (3 mL) was added and **9a** precipitated as a light gray solid which was isolated by filtration in a quantitative yield. The hydrogen atoms were labeled as described in ref.[12a] The ^{13}C-NMR signals were assigned by means of a C,H-COSY experiment. – **7a:** ^{1}H NMR (400 MHz, [D$_8$]THF, −50 °C): δ = 7.50−7.30 (m, 15 H, H_{Ph}), 5.54 [pseudo-sext, ^3J(1-H,4-H) = ^3J(1-H,5-H) = 12.7 Hz, ^3J(1-H,2-H) = 6.7 Hz, 1 H, 1-H], 5.05 (m, 1 H, 12-H), 4.66 (m, 1 H, 5-H), 4.27 [dd, ^3J(2-H,1-H) = 6.7 Hz, ^3J(2-H,P) = 3 Hz, 1 H, 2-H), 3.99 [pseudo-t, ^3J(13-H,12-H) = ^3J(13-H,P) = 8.6 Hz, 1 H, 13-H], 3.54 (m, 1 H, 14-H), 3.20 (m, 1 H, 4-H), 2.49 (m, 2 H, 7-H, 11-H), 2.38 (m, 1 H, 8-H), 2.09 (m, 1 H, 9-H), 1.45 (m, 1 H, 6-H), 0.97 (m, 1 H, 10-H). – ^{13}C{^{1}H} NMR (101 MHz, [D$_8$]THF, −50 °C): δ = 135−129 (C_{Ph}), 117.7 (C-2), 113.1 (C-7), 101.6 (C-3), 82.2 (C-8), 78.1 (C-1), 33.4 (C-5), 29.6 (C-4), 29.1 (C-6). – ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, −50 °C): δ = 24.94. – **9a:** ^{1}H NMR (400 MHz, [D$_8$]THF, −50 °C): δ = 7.50−7.10 (m, 30 H,H_{Ph}), 5.91 [pseudo-sext, ^3J(1-H,4-H) = ^3J(1-H,5-H) = 12.7 Hz, ^3J(1-H,2-H) = 6.7 Hz, 1 H, 1-H],

5.46 [pseudo-sext, ^3J(12-H,14-H) = 16.5 Hz, ^3J(12-H,13-H) = ^3J(12-H,10/11-H) = 6.7 Hz, 1 H, 12-H], 4.75 (m, 2 H, 13-H, 14-H), 4.48 (m, 1 H, 5-H), 3.53 (m, 2 H, 2-H, 4-H), 1.63, 1.50 (m, 6 H, 6-H to 11-H). – $^{31}P\{^1H\}$ NMR (162 MHz, [D_8]THF, −50 °C): AB spin system: δ_A = 24.68; δ_B = 24.26; $^2J(P_A,P_B)$ = 41.6 Hz.

[18] M. Brookhart, B. Grant, A. F. Volpe, Jr., *Organometallics* **1992**, *11*, 3920.

Received June 7, 1999
[I99208]