Biphasic Catalyzed Telomerization of Butadiene and Ammonia: Kinetics and New Ligands for Regioselective Reactions

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Abstract: The kinetics of the palladium-catalyzed biphasic telomerization of butadiene and ammonia by means of in situ catalysts consisting of phosphane palladium complexes were investigated at 80 °C. The effects of ligand, catalyst, and ammonia concentrations were studied. The rate of product formation as well as the regioselectivity of the reaction was found to depend greatly on ligand and catalyst concentration. A model for the reaction mechanism was deduced from these results, explaining the regioselectivities obtained. The regioselectivity could be strongly influenced by the ligand. We synthesized new water-soluble phosphanes with special π-acceptor/σ-donor properties for use in the telomerization reaction. TPPTS as a ligand gave the terminal octadienylamine with a regioselectivity of 50%, whilst a TPPTS derivative with three methoxy groups in ortho positions led to a regioselectivity of 94%. This corroborated the importance of ligand properties in this reaction.

Keywords: biphasic catalysis · kinetics · palladium · phosphanes · telomerization

Introduction

Telomerizations have proven to be of great industrial value,[1] and the products obtained play an important role as intermediate chemicals for the production of fine and bulk chemicals, depending on the nucleophile used. A large amount of work has been published on the influence of the catalysts, ligands and solvents on the activity and the selectivity of telomerizations.[2] Among these reactions, the telomerization of ammonia and butadiene (Scheme 1) has been extensively studied using homogeneously catalyzed single-phase reactions.[3] In this case, the main products obtained are the tertiary octadienylamines. The nucleophilicity increases in the order of ammonia, primary octadienylamine, and secondary octadienylamine so that the reaction cannot be stopped. A summary of all observed and possible products is given in Scheme 1.

We have shown that these consecutive reactions can be avoided by using the two-phase method,[4] which allows the selective production of the primary amines **1** and **2**. The reaction takes place in an aqueous catalyst phase and the primary products are extracted in situ by a second organic phase (e.g. toluene, methylene chloride, butadiene) which is immiscible with water. In order to optimize and better understand the regioselectivity and the rate of the product formation, we investigated the kinetics of this reaction. The kinetic experiments led to a model of the reaction that also explains the different regioselectivities. We then investigated ligand variations to control the regioselectivity of the reaction. The kinetic results, several new ligands, and a novel palladium complex will be presented in this paper.

Results and Discussion

At first we determined the influence of diffusion and mass transport phenomena and found that with the reactor described in the experimental section (Figure 4), the stirring velocity must be set to at least 1200 rpm to ensure a thorough mixing of the two phases (aqueous catalyst phase/liquid butadiene). To avoid any diffusion problems and to ensure proper mixing, the stirring velocity was kept at 2500 rpm throughout all experiments. In order to define a reasonable starting point for the reaction, all reactants must be present, the catalyst must be in its active form, and the reaction temperature must be set. Since the first step of the catalyst formation is the coordination of TPPTS (TPPTS = 3,3′,3″-phosphinidynetris(benzenesulfonic acid) trisodium salt) to palladium acetate followed by a reduction of the palladium(II) compound to a palladium(0) complex, as shown in Scheme 2, the catalyst formation was given 15 min to proceed at 80 °C (as one equivalent of phosphane is consumed in this reaction, all following plots and discussions are corrected, and the

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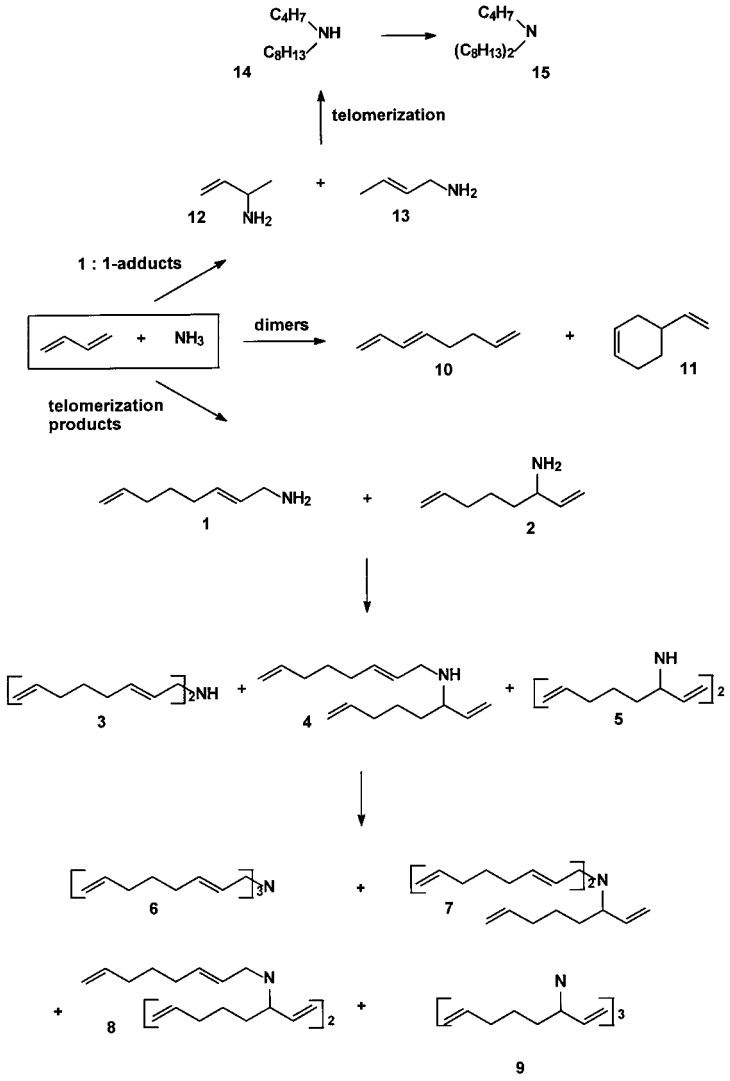

Scheme 1. Main and by-products in the telomerization of butadiene and ammonia.

Abstract in German: *Es wurden kinetische Untersuchungen zur Zweiphasentelomerisation von Butadien und Ammoniak in Gegenwart wasserlöslicher In-situ-Katalysatoren aus Palladiumacetat und Phosphanen bei 80°C durchgeführt. Die Einflüsse der Liganden-, Katalysator- und Ammoniakkonzentrationen wurden ermittelt. Die Produktbildungsgeschwindigkeiten und die Regioselektivität der Reaktion hängen entscheidend vom Ligand/Palladium-Verhältnis und von der Katalysatorkonzentration ab. Aus diesen kinetischen Untersuchungen wurde ein Modell zur Beschreibung des Reaktionsmechanismus abgeleitet, mit dem die erhaltenen Regioselektivitäten erklärt werden können. Die Regioselektivität wird entscheidend vom Phosphanliganden beeinflußt. Wasserlösliche Phopshane mit speziell auf diese Telomerisation abgestimmten π-Akzeptor/σ-Donor-Eigenschaften wurden hergestellt, darunter auch zwei neue. Der TPPTS-Ligand führt zur Bildung des terminalen Octadienylamins mit einer Regioselektivität von 50%, während ein TPPTS-Derivat mit drei ortho-ständigen Methoxygruppen zur Bildung des terminalen Octadienylamins mit einer Regioselektivität von 94% führt. Diese Ergebnisse belegen den Einfluß der Ligandeneigenschaften in dieser Reaktion.*

amounts of phosphane given are those present after catalyst formation).

Studies of the analogous reaction with palladium acetate and triphenylphosphane by Amatore et al.[5] show that the half-time for catalyst formation is 106 seconds at 60°C. Therefore, all reactants except ammonia were placed in the reactor, which was then heated to reaction temperature (80°C). After 15 min of stirring at 80°C, the ammonia was added. Since ammonia and butadiene are present in large excess, the concentrations can be considered as constant. The same should be true for the product concentrations, since the products are extracted into the butadiene phase immediately, that is, no consecutive reactions are possible at the beginning of the reaction. Since the amount of ammonia introduced into the reactor is small enough for the temperature to return to 80°C only 2 min after the addition, we assume that any concentration changes are negligible and define the starting point of the reaction as 2 min after the addition of ammonia. Samples of the reaction mixture were taken

$$Pd(OAc)_2 + (n{+}1)\,PR_3 \rightarrow [Pd(OAc)_2(PR_3)_2] \rightarrow [Pd(PR_3)_n] + R_3P{=}O$$

Scheme 2. Reduction of $Pd(OAc)_2$ by PR_3 (R = *m*-sulfonatophenyl).

at regular intervals and the amount of amines **1** and **2** was analyzed. A typical plot of the obtained amounts of **1** and **2** with respect to time is shown in Figure 1.

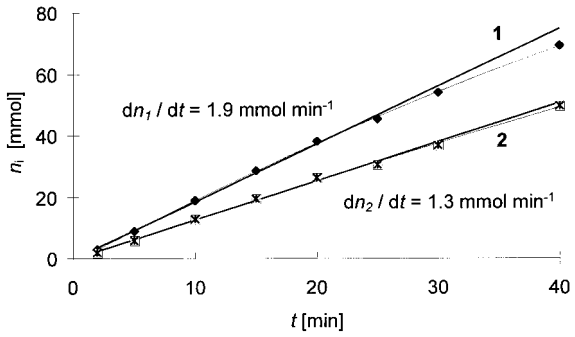

Figure 1. Typical reaction plot of the telomerization of butadiene and ammonia (conditions: 100 mL water; 9.7 g ammonia; 170 g butadiene; 0.5 mmol $Pd(OAc)_2$; 1.12 mmol TPPTS; $T = 80°C$).

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Effect of the amount of TPPTS: The results of the variation of the amount of TPPTS are shown in Figure 2. To simplify the discussion, the rate of the product formation d*n*/d*t* is plotted against the TPPTS/Pd ratio. For both **1** and **2**, the reaction rate

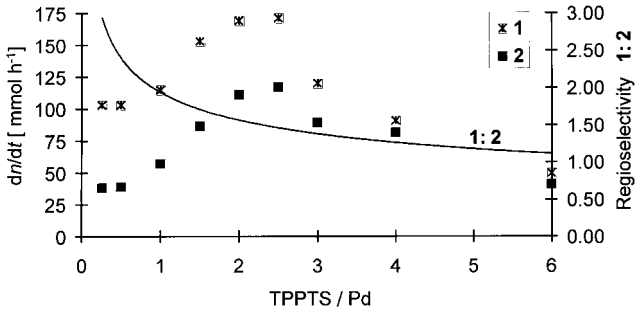


Figure 2. Rate of primary amine formation d*n*/d*t* and regioselectivity ratio of **1**:**2** plotted versus the TPPTS/Pd ratio (conditions: 100 mL water; 25 g ammonia; 170 g butadiene; 0.375 mmol $Pd(OAc)_2$; $T = 80\,^{\circ}C$).

reaches a maximum for TPPTS/Pd ratios of 2–2.4. The turnover frequency (TOF) plot, which was omitted in Figure 2 for clarity, looks similar since the amount of palladium used is the same at all data points. The largest value of the TOF was 768 at a TPPTS/Pd ratio of 2.4. The solid line, which shows the regioselectivity ratio of **1**:**2**, clearly indicates that the regioselectivity strongly depends on the catalyst composition. Low amounts of TPPTS strongly favored the formation of **1**, whereas **2** was produced in large amounts at high amounts of TPPTS. At a TPPTS/Pd ratio of 6, both **1** and **2** were formed in almost identical quantities.

Effect of the amount of catalyst: The total catalyst amount was varied, leaving the TPPTS/Pd ratio constant. The rates of product formation and the ratio of **1** to **2** are plotted in Figure 3 versus the amount of catalyst used. At very small catalyst amounts, the reaction rate increased only moderately

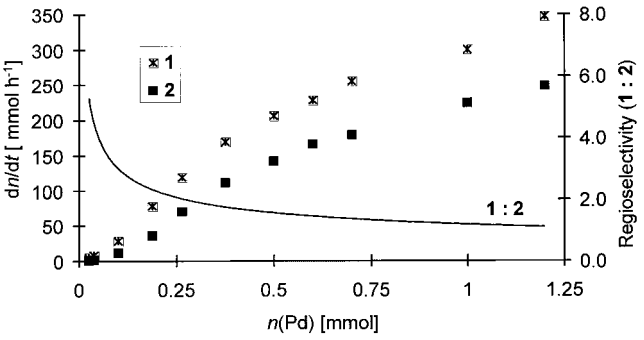


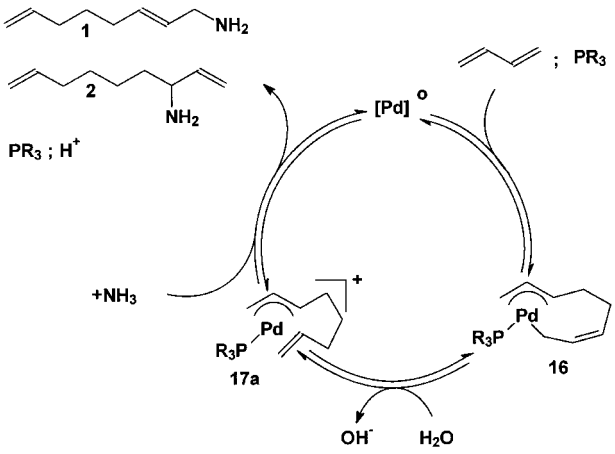
Figure 3. Rate of product formation and regioselectivity versus catalyst amount (conditions: 100 mL water; 25 g ammonia; 170 g butadiene; Pd/TPPTS = 1:2; $T = 80\,^{\circ}C$).

with increasing amounts of catalyst, whereas at catalyst amounts of 0.25–0.5 mmol, the slope of the curve was much steeper: in this region, a doubling of the catalyst amount resulted in a doubling of the reaction rates. At higher catalyst amounts, the increase of the reaction rates was lower. These findings were reflected by the TOF, which increased strongly at medium amounts of catalyst and decreased at high catalyst amounts. At small amounts of catalyst, the product ratio **1**:**2** was almost 6. However, the regioselectivity dropped rapidly and came close to 1 when the catalyst amount was 1 or higher.

Effect of the amount of ammonia: When the amount of ammonia was varied, a quantitative comparison with the results described above was not possible, as the experiments concerning the amount of TPPTS and catalyst rely on the constancy of the amounts of butadiene and ammonia. Nevertheless, we varied the amount of ammonia to gain a qualitative impression. The main trends observed are: increasing the ammonia amount from 0.5 to 2.75 equivalents led to an increase in the regioselectivity from ca. 1.5–2.1 (**1**:**2** ratio), whereas the reaction rate increased at first, reached a maximum at ca. 1 equiv of ammonia and then dropped again.

Deduction of a model of the reaction mechanism: Various models explaining the reaction mechanism of telomerizations have been published, although none of them describe the observed regioselectivities. Two generally different models have been discussed, one involving mononuclear palladium species, the other favoring dinuclear palladium species. Additionally, a model involving a palladium hydride species has been published. These models were compared in a review by Behr.[2]

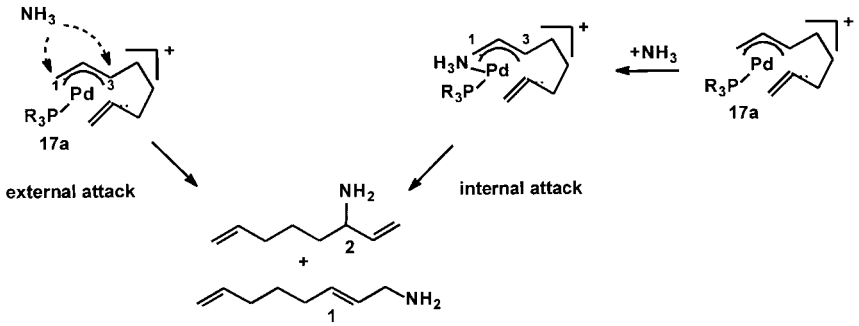
On the basis of our kinetic studies, we consider a mechanism involving a mononuclear palladium species to be active, which also explains the observed regioselectivities. In Scheme 3 we propose a catalytic cycle, which was developed in accordance with the cycle postulated by Jolly et al.[6] They studied telomerizations with other nucleophiles and have presented experimental proof for this type of catalytic cycle.



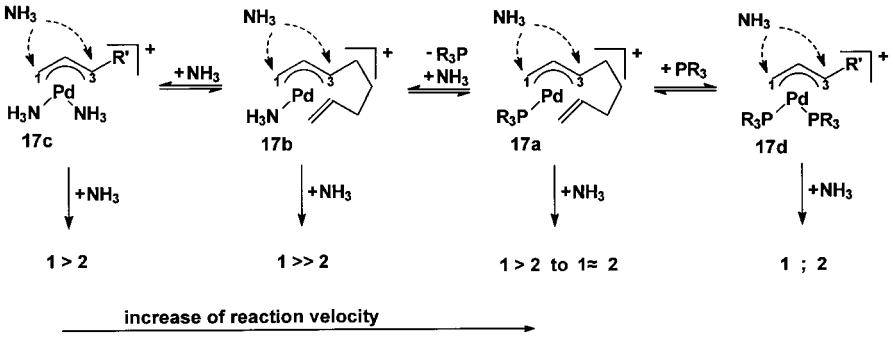
Scheme 3. Model of the catalytic cycle for the telomerization of butadiene and ammonia.

A palladium(0) species first forms complex **16** with butadiene and TPPTS, which is transferred to **17a** by protonation. Ammonia as the nucleophile then attacks **17a**, thus, after removal of a proton, resulting in the formation of **1** and **2**. During this reaction, the palladium(0) species and the ligand are released. The palladium(0) species then reacts with TPPTS

and butadiene to start the cycle again. To explain the regioselectivities it is necessary to study the nucelophilic attack of ammonia on **17a**. According to Scheme 4 it should first be decided whether the ammonia enters the molecule by external or internal attack. According to Trost and Van Vranken[7] the pK_a value of the corresponding acid of a soft nucleophile, which prefers external attacks, is lower than 25. Ammonia is thus a soft nucleophile entering **17a** by an external attack. Since the amount of TPPTS has a drastic influence on the regioselectivity, it is most probable that **17a** is part of a complex equilibrium shown in Scheme 5.



Scheme 4. Internal and external attack of ammonia on complex **17a**.



Scheme 5. Equilibria between different palladium complexes on which the nucleophilic attack of ammonia takes place: a model of how to govern the regioselectivity.

Assuming that all four complexes **17a**–**17d** undergo reactions with ammonia and that the regioselectivities for the nucleophilic attack are different for each of these complexes, the overall regioselectivity should depend on these equilibria and thus on the TPPTS concentration. To estimate this influence, we will first discuss the regioselectivities which one would expect for any of **17a**–**17d**.

The palladium center in **17a**–**17d** has a d^8 configuration, which makes it reasonable to assume that the structures are square planar. In complexes of this type, the electronic influence of one ligand upon another is very strong if the two ligands are in the *trans* position to each other. π-acceptor ligands like alkenes and phosphanes will reduce the electron density at the palladium center, and this effect will be passed on to the ligand in the *trans* position. Pure σ-donor ligands like ammonia will not diminish the electron density at a ligand *trans* to it.

If steric effects are excluded, ammonia should attack **17a**–**17d** at the carbon center with the lowest electron density. This step should be faster when the electron density is generally lower in the allyl group. Following these considerations, **17c** should react very slowly since no π-acceptor ligands are present. The C-1 position may be slightly favored for an attack, since there is less steric hindrance compared to C-3. Additionally, C-3 should prove to have a somewhat higher electron density owing to the alkyl chain attached to it. The olefinic double bond coordinating in **17b** should produce a considerably lower electron density at C-1. A nucleophilic attack should therefore be preferred at this position and be faster than in **17c**. If ammonia in **17b** is replaced by PR_3, one obtains **17a**, a complex with two π-acceptor ligands, which should consequently react faster than **17b**. It is reasonable to assume that the regioselectivity in this complex depends on the strength of the π-acceptor properties of the phosphane: the higher the π-acceptor ability of the phosphane, the higher the probability of an attack at C-3. If even more phosphane is present, a second phosphane replaces the coordinating olefinic group and **17d** is obtained. Compared with **17b** and **17c**, this complex should be very reactive since it also contains two π-acceptor ligands. As with **17c**, an attack at C-1 should be slightly favored.

The experimental results clearly reflect these considerations:a) Much more **1** than **2** is produced at low TPPTS concentrations, the predominant equilibrium species being **17c** and **17b**, which favor attack at C-1. Rising TPPTS concentrations diminish the **1**:**2** ratio, reflecting the fact that differentiation between C-1 and C-3 is much smaller, with the overall reaction being faster. The decrease in activity, which is observed when the TPPTS concentration exceeds 2.5 equiv, cannot be explained with this model, but an excess ligand will favor the formation of the catalytically inactive $[Pd(TPPTS)_3]$.[8]

b) At low catalyst concentrations, the equilibrium lies on the side of **17c** and **17b**, which favors the formation of **1**. Since the ammonia concentration as well as the Pd/TPPTS ratio is constant, the equilibrium is shifted to **17a** and **17d** as well as $[Pd(TPPTS)_3]$ with rising catalyst concentrations, resulting in a decrease of the **1**:**2** ratio.

c) Rising ammonia concentrations shift the equilibrium towards the formation of **17b** and **17c**. Accordingly, the activity is diminished whereas the selectivity is increased. If the ammonia concentration is low, the more active **17a** and **17b** complexes are the predominant species, resulting in faster reactions and a diminished selectivity to **1**. If the ammonia

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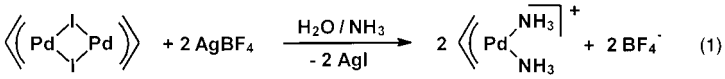
concentration is very low, activity decreases again, since at such low concentrations the ammonia concentration is directly part of the rate law for nucleophilic attacks on all four complexes **17a**–**17d**.

Ligand variations: Several water-soluble ligands with different σ-donor/π-acceptor properties have been used in this reaction in order to prove the model described above on how to steer the regioselectivity.

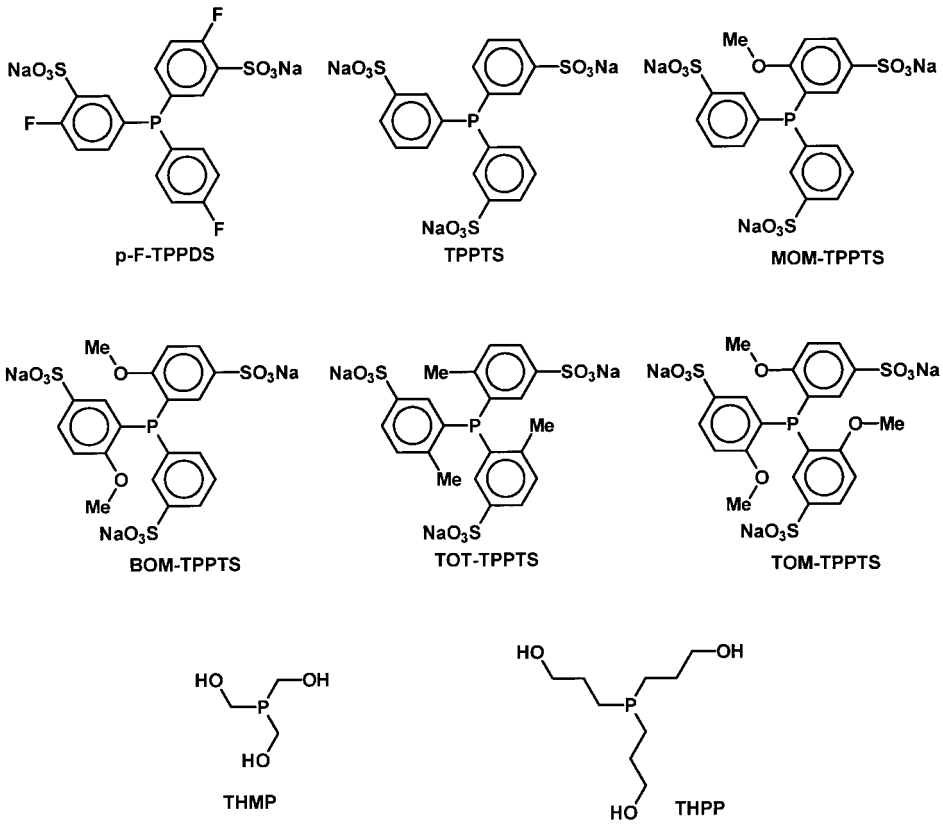
The generation of the active catalyst starting from $[Pd(OAc)_2]$ and a monodentate phosphane has some disadvantages. One equivalent of the phosphane is oxidized to phosphane oxide and stays in the catalyst solution. Furthermore, the properties of ammonia as ligand without any phosphanes cannot be tested with palladium acetate. Therefore, we looked for a new catalyst preformation and synthesized a new palladium complex appropriate for our reaction. The synthesis is depicted in Equation (1).



(1)

The new complex **19** was characterized by NMR and IR spectroscopy and elemental analysis (see Experimental Section). Compound **19** has already been proposed in theoretical investigations.[9] The reaction of the complex with ligand and butadiene may follow the sequence shown in Scheme 6. Both methods of catalyst preparation, one starting from palladium acetate and phosphane and the other starting from the new allyl complex and phosphane, were compared. The catalytic results are identical concerning activity and selectivity in the telomerization.

We synthesized several ligands with different σ-donor/π-acceptor properties and looked for their influence on the regioselectivity and activity in the telomerization of butadiene and ammonia. The ligands MOM-TPPTS and BOM-TPPTS were synthesized and characterized for the first time following published procedures.[10] In agreement with Tolman's IR studies of $[Ni(CO)_3PR_3]$ complexes,[11] the σ-donor properties of the used ligands should increase in the following order: *p*-F-TPPDS, TPPTS, MOM-TPPTS, BOM-TPPTS, TOT-TPPTS, TOM-TPPTS, THMP, THPP. These phosphanes are shown in Scheme 7.

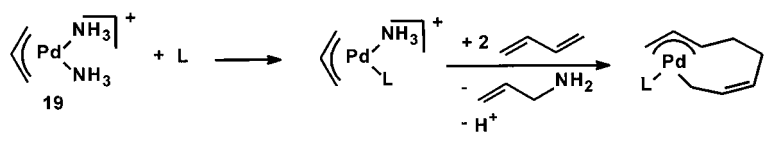


Scheme 7. Phosphane ligands used for the telomerization of butadiene and ammonia.

On the basis of our model of how to govern the regioselectivity of the nucleophilic attack, we expected the ligands with stronger σ-donor properties to lead to a higher selectivity for the terminal amine **1**. The electron density at C-3 of the allyl group should be higher than the electron density at C-1 so that the nucleophilic attack at C-1 is more favored. Furthermore, the activity of the palladium phosphane complexes should decrease with increasing σ-donor properties of the ligand. The catalytic results for the eight phosphanes as ligands in the palladium-catalyzed telomerization of butadiene and ammonia are summarized in Table 1.

The aryl phosphanes (numbers 1–6) gave the results we expected. *p*-F-TPPDS has the strongest π-acceptor properties and has the highest activity compared with all other tested ligands (number 1). The selectivity for the terminal amine **1** is rather low at 54%. With increasing σ-donor properties the selectivities for **1** increase and the activity decreases. The best results in obtaining the desired product **1** were reached with TOT-TPPTS (number 5) and TOM-TPPTS (number 6). These ligands have the highest σ-donor properties and yield 91 and 94% of product **1**; the activities, however, remain low. The turnover frequency is only around 46 h^{-1}.

The catalytic results of the hydroxyalkylphosphanes (numbers 7 and 8) are different. No reaction takes place with the



Scheme 6. Possible generation of the active species starting from **19**.

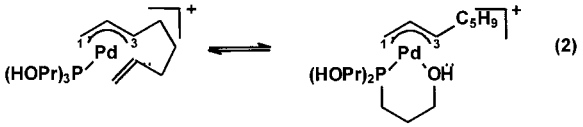
Table 1. Influence of phosphanes with different electronic properties on the regioselectivity and activity in the telomerization of butadiene and ammonia. Conditions: $T = 80\,^{\circ}C$, $t = 0.75$ h, $n(Pd) = 0.113$ mmol, Pd:phosphane = 1:1, c(ammonia) = 27 weight %, 30 mL aq. NH_3, 40 g butadiene.

No.	Phosphane	Selectivity			Regio-selectivity	TOF [h^{-1}]
		1	**2**	**3–5**	(**1**:**2**)	
1	*p*-F-TPPDS	54	38	6	1.4	357
2	TPPTS	76	21	3	3	252
3	MOM-TPPTS	70	22	7	3.2	263
4	BOM-TPPTS	87	7	5	13	128
5	TOT-TPPTS	91	5	1	18	46
6	TOM-TPPTS	94	3	1	36	47
7	THMP[a]	–	–	–	–	–
8	THPP[b]	85	9	3	8.7	14

[a] $t = 15$ h. [b] $t = 4$ h.

ligand tris(hydroxymethyl)phosphane (THMP), even after 15 h (number 7). This ligand is thermally labile and decomposes by elimination of formaldehyde, so we ran the reaction at 60 °C. Even at this temperature and at higher ligand concentrations, no telomerization occurs. We are surprised that a recent publication describes the telomerization of butadiene and water with this ligand.[12]

Tris(3-hydroxypropyl)phosphane (THPP) is an active ligand in the telomerization of butadiene and ammonia, but the selectivity for **1** is lower than expected (number 8). The reason for this low selectivity of 85 % may depend on the coordination ability of the ligand, as depicted in Equation (2). One



(2)

hydroxy function of the phosphane may coordinate to palladium and hinder the olefinic group from coordinating. The two palladium species may be in equilibrium and this may be the reason for the regioselectivity ratio of 8.7.

These experiments with different ligands show that our mechanistic model is suitable to explain the regioselectivity and activity of the palladium-catalyzed telomerization of butadiene and ammonia. We were able to synthesize water-soluble phosphanes that gave high amounts of the terminal amine.

Recycling of the catalyst: As well as the selectivity, the total turnover number (TON) of a catalyst system is very important for reactions which are of industrial interest, such as the telomerization of butadiene and ammonia. We therefore tried to recycle the catalyst and discuss the results here.

The recycling experiments were done with $Pd(OAc)_2$/TPPTS in different ratios. The product phase was separated after each run and the aqueous catalyst phase was directly introduced into the reactor again. The results are summarized in Table 2. The results show that catalyst recycling is generally possible. With four equivalents of TPPTS, there is a small increase in activity from the first to the third run followed by a little decrease in the fourth run (numbers 1–4). The catalyst

Table 2. Recycling of the catalyst system $Pd(OAc)_2$/TPPTS. Conditions: $T = 80\,^{\circ}C$, $t = 1$ h, c(ammonia) = 27 weight %, 30 mL aq. NH_3, 40 g butadiene, 0.113 mmol Pd.

No.	Run	TPPTS/Pd[a]	Selectivity			TOF [h^{-1}]	TON
			1	**2**	**3–5**		
1	1	4:1	50	45	3	140	140
2	2	4:1	49	43	5	215	355
3	3	4:1	47	40	8	302	657
4	4	4:1	46	41	7	267	924
5	1	2:1	55	37	7	577	577
6	2	2:1	53	36	10	468	1045
7	3	2:1	53	31	15	421	1466
8	4	2:1	54	28	16	192	1658

[a] Pd/ligand ratio after catalyst preformation.

system with two equivalents of TPPTS shows a drastic decrease of activity after the first run already. The ratio of the primary amines **1**:**2** increases from run to run, favoring the formation of the terminal amine **1**. These results indicate that the amount of TPPTS in the catalyst phase decreases from run to run. We took small samples of the catalyst phase after each run and analyzed them by ^{31}P NMR. The NMR spectra show that the integrated signal for the TPPTS oxide ($\delta = 35$ ppm) increases compared with the integrated signal for coordinated TPPTS ($\delta = 24-25$ ppm), which decreases from run to run. In summary, the NMR experiments underline the assumption that the phosphane TPPTS is converted to the phosphane oxide during the catalytic reaction.

The selectivity for secondary amines increases continuously. This phenomenon indicates that the catalyst leaches into the organic phase where it catalyzes the reaction of primary amines with butadiene to yield the secondary amines. This effect may also be explained by the oxidation of TPPTS.

Conclusions

The kinetics of the catalytic biphasic telomerization of butadiene and ammonia with water-soluble palladium catalysts were investigated at 80 °C. It was shown that the concentrations of TPPTS, ammonia, and catalyst significantly influenced the reaction rate as well as the regioselectivity. The higher the ligand concentration and the catalyst concentration, the faster the reaction. This is explained by the π-acceptor properties of the TPPTS ligand, which diminish the electron density in the allyl group and thus make the latter more reactive towards nucleophilic attack. The observed regioselectivities are certainly a result of the combination of steric and electronic effects, but we believe that the general trend is that pure σ-donors lead to higher electron densities at the carbon center in the *trans* position than σ-donor–π-acceptor ligands like olefins and phosphanes. The last two diminish the electron density at the carbon center mentioned above, thus favoring attack at this position. This explanation is based on a complex equilibrium, every single species being active in the telomerization. High selectivities towards amine **1** are generally observed with low catalyst concentrations and low TPPTS amounts. The electronic properties of phosphanes have an important influence on the activity and regioselectivity in the telomerization.

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Eight different water-soluble phosphanes were compared. The ligand with the highest π-acceptor properties (*p*-F-TPPDS) gave the lowest selectivity to the terminal amine **1** whereas the ligand with the highest σ-donor properties (TOM-TPPTS) led to **1** with a selectivity of 94%. Lowering the π-acceptor properties of the ligand decreased the activity of the catalyst system.

In addition to the ligands known from the literature, we synthesized two new ligands, mono(orthomethoxy)-TPPTS and bis(orthomethoxy)-TPPTS, and one new palladium complex [(allyl)Pd$(NH_3)_2$](BF_4). Finally, we tried to recycle the catalyst by simple phase separation. The phosphane was oxidized during recycling; this caused a decrease in activity. The amount of secondary amine increased from run to run, probably because the palladium complex leached into the organic phase. In general, catalyst recycling was possible.

Experimental Section

Materials: All reactions and handling were done under dried argon. Palladium acetate [$Pd(OAc)_2$] was used without further purification. Butadiene and ammonia were taken from conventional tanks. Undecane was used as an internal standard for the gas chromatographic characterization of the reaction mixture. TPPTS was used as a 32.4% aqueous solution, which was supplied by Bayer AG. THPP was synthesized following a patented procedure[13] and was purified by column chromatography.[14] THMP,[15] *p*-F-TPPDS,[16] TOM-TPPTS, and TOT-TPPTS[10] were synthesized following literature procedures. The syntheses of MOM-TPPTS and BOM-TPPTS are new and are described below.

Synthesis of MOM-TPPTS: A solution of H_3BO_3 (4.38 g) in concentrated sulfuric acid (41 mL, deoxygenated) was introduced into a three-necked flask under argon. *ortho*-(Methoxyphenyl)diphenylphosphane (5 g) was added and the whole solution was cooled down to −10 °C. At this temperature, oleum (73.9 mL, 65% SO_3) was added through a dropping funnel over 2 h. This solution was stirred at room temperature for 3 days. Before continuing the synthesis by hydrolysis, a small sample of 5 mL was taken to test the degree of sulfonation by ^{31}P NMR analysis. When the reaction time was too short, mono- and disulfonated products were found. The amount of phosphane oxide was very high when the reaction time was too long. It was very difficult to separate all the products. The flask was cooled by ice during the addition of deoxygenated water (50 mL). The whole reaction mixture was then introduced into a 2 L Schlenk flask. The mixture was neutralized with a NaOH solution (7.5 mol) and cooled with ice. The pH value, which must reach 7, was monitored by a pH electrode. The solution was evaporated and the product extracted with methanol (250 mL). This solution was filtered over Celite and the methanol evaporated in vacuo. The residue was dissolved in water (20 mL) and filtered over a syringe filter, and the water was evacuated. The product was isolated in a purity of 93% with a yield of 14% after several extractions with methanol and water. For characterization, the ligand was purified by subsequent gel MPLC.

Characterization of MOM-TPPTS: ^{31}P NMR (121 MHz, D_2O, 25 °C, H_3PO_4): $\delta = -14.62$; ^1H NMR (300 MHz, D_2O, 25 °C, TMS): $\delta = 3.6$ (s, 3H, OCH_3), 6.96 (m, 1H, *ortho* position to methoxy), 7.02 (m, 1H, *meta* position to methoxy), 7.3 (dd, 2H, $^3J(H,H) = 7.5$ Hz, $J(P,H) = 7.5$ Hz), 7.4 (dd, 3H, $^3J(H,H) = 7.5$ Hz, $J(H,H) = 7.5$ Hz), 7.6 (d, 2H, $^3J(H,H) = 7.5$ Hz), 7.71 (m, 3H, H in *ortho* position to the sulfonate group); ^{13}C NMR (75 MHz, D_2O, 25 °C, TMS): $\delta = 164.2$ ($J(P,C) = 13.7$ Hz), 144.6 ($J(P,C) = 7.7$ Hz), 138.1 ($J(P,C) = 17.4$ Hz), 137.06; 137.1 ($J(P,C) = 9$ Hz), 132.25 ($J(P,C) = 3.7$ Hz), 131.9 ($J(P,C) = 24$ Hz), 131.2 ($J(P,C) = 6.4$ Hz), 130.8, 128.2, 125.7 ($J(P,C) = 11$ Hz), 112.9, 57.7; IR (KBr): $\tilde{\nu} = 3071.9$ (C–H aryl), 2840.9 (O–CH_3 methoxy), 1642.2, 1582.1, and 1475.5 (C=C aryl), 1402 and 1147.7 (SO_3Na), 1194.2 (ArC–O–C), 853.6, 814.8, and 791.6 cm^{-1} (δ C–H aryl); elemental analysis calcd for $C_{19}H_{20}O_{13}S_3Na_3$ (621.5): C 34.98, H 3.09; found: C 35.5, H 2.96.

Synthesis of BOM-TPPTS: The synthesis was carried out in the same way as described for MOM-TPPTS, the (*ortho*-methoxyphenyl)diphenylphosphane being substituted by bis(*ortho*-methoxyphenyl)phenylphosphane. The ligand was isolated in a yield of 15% and a purity of 92%. For characterization, the ligand was purified by gel MPLC.

Characterization of BOM-TPPTS: ^{31}P NMR (121 MHz, D_2O, 25 °C, H_3PO_4): $\delta = -24.34$; ^1H NMR (300 MHz, D_2O, 25 °C, TMS): $\delta = 3.63$ (s, 6H, 2 OCH_3), 7.0 (dd, 2H, *ortho* position to methoxy, $^3J(H,H) = 4.7$ Hz, $J(H,P) = 8.7$ Hz), 7.03 (dd, 2H, *meta* position to methoxy, $^3J(H,H) = 4.7$ Hz, $^3J(H,H) = 2.3$ Hz), 7.32 (dd, 1H, $^3J(H,H) = 7.5$ Hz, $J(P,H) = 7.5$ Hz), 7.42 (dd, 1H, $^3J(H,H) = 7.5$ Hz, $^3J(H,H) = 8.5$ Hz), 7.63 (d, 1H, $^3J(H,H) = 8.5$ Hz), 7.73 (m, 3H, H in *ortho* position to the sulfonate group); ^{13}C NMR (75 MHz, D_2O, 25 °C, TMS): $\delta = 161.7$ ($J(P,C) = 14.2$ Hz), 141.9 ($J(P,C) = 8.6$ Hz), 135.5 ($J(P,C) = 16.7$ Hz), 134.4, 133.55 ($J(P,C) = 8$ Hz), 129.6, 129.4 ($J(P,C) = 23$ Hz), 128.5 ($J(P,C) = 6.3$ Hz), 128, 125.6, 121.8 ($J(P,C) = 10$ Hz), 110.25, 55.0; IR (KBr): $\tilde{\nu} = 3075.6$ (C–H aryl), 2841.4 (O–CH_3 methoxy); 1653.1, 1581.2, and 1477.1 (C=C aryl), 1386 and 1140.1 (SO_3Na), 1194.7 (ArC–O–C), 840.3, 823, and 790.8 cm^{-1} (δ C–H aryl); elemental analysis calcd for $C_{20}H_{22}O_{14}S_3Na_3$ (651.6): C 35.2, H 3.25; found: C 36.3, H 3.41.

Preparative gel-MPLC for ligand purification: This method offered the possibility of purifying sulfonated ligands and eliminating inorganic byproducts (Na_2SO_4) as well as isolating phosphane oxides from phosphane. The procedure was first published by Herrmann et al.[17] We used a glass column of diameter 2.6 cm and length 60 cm. The stationary phase was Toyopearl HSK 40 by Tosohaas and the eluent was deoxygenated water. The chromatography was performed with a Novaprep apparatus from Septech/Merck in combination with an RI detector.

200 mg of the ligand was dissolved in 2.5 mL water, which was then introduced into the column. The eluent velocity was kept constant at 3 mL min^{-1}. In all cases, the phosphane oxide left the column first followed by the phosphane. Retention times depended on the packing of the column and lay within a range of 2 h for all ligands. The fraction that contained the ligand was introduced into a Schlenk flask and the water was evaporated.

Synthesis of [η^3-allyldiaminopalladium(tetrafluoroborate)]: [Bis-(η^3-allyl-iodopalladium)] (1372 mg) was dissolved in aqueous 27% ammonia solution (10 mL). This solution was added to a solution of $AgBF_4$ (973.4 mg) in water. The precipitated silver iodide was filtered off over Celite. The filtrate was evaporated and the residue extracted three times with 10 mL hot methylene chloride. The combined methylene chloride phases were cooled to −30 °C and the rest of the product was crystallized by the addition of 20 mL pentane. The white product was washed three times with 5 mL pentane and dried in vacuo. The yield was 50.3%.

Characterization: ^1H NMR (300 MHz, D_2O, 25 °C, TMS): $\delta = 2.9$ (d, 2H, $^3J(H,H) = 12.3$ Hz), 3.97 (d, 2H, $^3J(H,H) = 7.2$ Hz), 5.5 (m, 1H); ^{13}C NMR (75 MHz, D_2O, 25 °C, TMS): $\delta = 61$ and 118; IR (KBr): $\tilde{\nu} = 3383.8$ and 3308.9 (N–H), 1616.9 (δ NH), 1386.9 (δ_{as} CH_2), 1301.1 (δ_{sym} CH_2), 1051.3 ($\tilde{\nu}$ C–C–C), 523.4 cm^{-1} (δ C–C–C); elemental analysis calcd for $C_3H_{11}N_2PdBF_4$ (268.3): C 13.43, H 4.13, N 10.44; found: C 13.71, H 4.10, N 10.16.

Experimental setup: All telomerizations for the kinetics were carried out in a 1000 mL reactor, which was built in the workshop of our institute. A schematic representation of the autoclave and the complete setup is shown in Figure 4. The reactions to compare the different ligands were run in a 125 mL reactor with an appropriate stirrer.

Experimental procedure for telomerization: The reactor was first evacuated and filled with argon three times. H_2O (60 mL) and undecane (ca. 5 mL) were then introduced (the exact amount was determined by a syringe and with the help of the mass difference of the autoclave). The correct amounts of palladium acetate and TPPTS were introduced into a Schlenk vessel, dissolved with H_2O (40 mL) and transferred to the reactor. Butadiene (170 g) and the desired amount of ammonia were condensed into dosing cartridges. The exact amounts were transferred to the autoclave by releasing the pressure on the cartridges. The exact amount of butadiene was determined by mass difference (difference between full and empty cartridge). The two-phase system (aqueous catalyst phase and liquid butadiene) in the reactor was stirred at 2500 rpm and was electrically heated to reaction temperature. The reaction mixture was stirred for 15 min at reaction temperature to ensure the preformation of the active catalyst species from the two components (palladium precursor and ligand) before

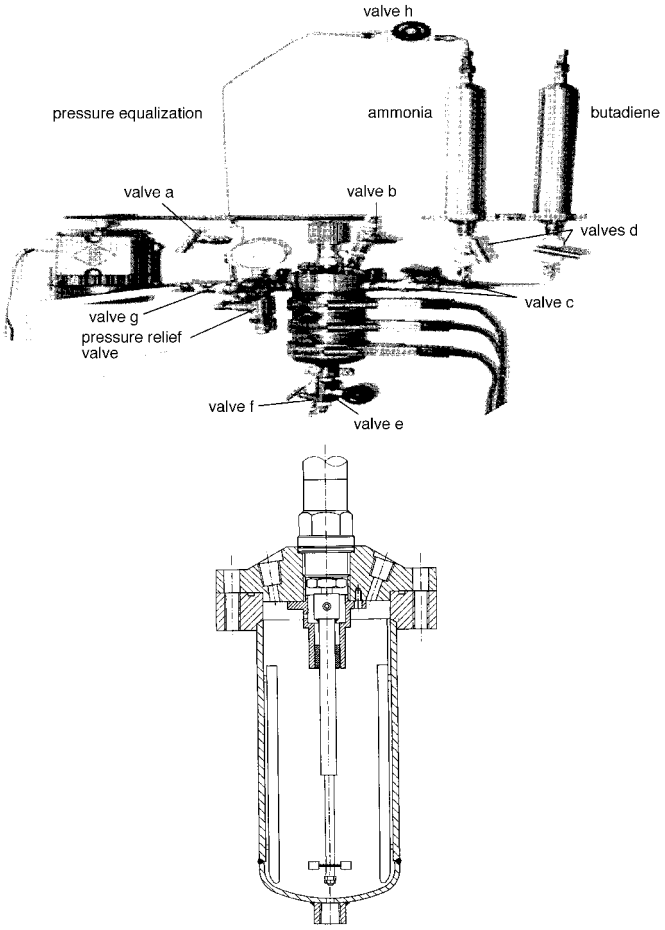

Figure 4. Photograph of the apparatus and diagram of the reactor.

ammonia was added. The starting point of the reaction was defined by the addition of ammonia. After 2 min, the first sample was taken through a valve connected to a steel capillary with a diameter of 1 mm. This capillary led into a test tube that was cooled by ice. The volume of the sample was 2 mL. 2 mL of the reaction mixture was flushed through the capillary before each fresh new sample was taken. 1 mL of toluene was then added to the sample and mixed thoroughly. The phases were separated, and the organic phase was dried over a 4 Å molecular sieve and analyzed by GC. Further samples were taken after 5, 10, 15, 20, 25, 30 and 40 min reaction time. Once the reaction was finished, the unreacted butadiene was burned with a bunsen burner.

Interpretation of the kinetic experiments: The amount of the primary amines **1** and **2** were determined for the different reaction times from the GC chromatograms of the eight samples. All the values are put together in a diagram from which the upward gradient of the reaction in the starting phase was determined by a linear regression analysis. This gradient is equivalent to the reaction velocity in the starting phase. The reaction parameters and the reaction velocities in the starting phase are summarized in Table 3.

Analytical methods: The GC chromatograms were recorded on a Sichromat 1 apparatus (Siemens). The detector was a FID and the integrator used was a HP-LAS 3359. The conditions were: column: 50 m Pona-HP-FS; temperature program: 5 min isotherm at 50 °C, 5 °C min^{-1} to 150 °C, 20 °C min^{-1} to 259 °C; temperature of the evaporator: 200 °C; H_2, 1.5 bar; sample volume: 0.3 – 1.0 μL.

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Table 3. Reaction parameters and corresponding reaction velocities.

$n(NH_3)$ [mol]	n_0(Pd) [mmol]	n_0(TPPTS) [mmol]	dn(**1**)/dt [mol h^{-1}]	dn(**2**)/dt [mol h^{-1}]
1.38	0.025	0.085	0.005	0.0008
1.38	0.0379	0.116	0.008	0.0016
1.38	0.1	0.3	0.029	0.011
1.38	0.188	0.615	0.078	0.036
1.38	0.264	0.821	0.119	0.071
1.38	0.375	1.13	0.169	0.111
1.38	0.55	1.5	0.206	0.142
1.38	0.6	1.8	0.228	0.166
1.38	0.7	4.8	0.261	0.179
1.38	0.375	0.473	0.103	0.038
1.38	0.375	0.562	0.103	0.039
1.38	0.374	0.753	0.115	0.057
1.38	0.0374	0.936	0.153	0.086
1.38	0.375	1.31	0.171	0.117
1.38	0.377	1.49	0.12	0.089
1.38	0.376	1.88	0.091	0.081
1.38	0.375	2.63	0.05	0.041
2.72	0.5	1.0	0.119	0.058
0.57	0.5	1.12	0.113	0.076
1.81	0.5	1.1	0.147	0.084
1.14	0.5	1.1	0.162	0.094
1.38	1.0	3.1	0.3	0.224
1.38	1.2	3.6	0.374	0.248

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