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Efficient catalysts for telomerization of butadiene with amines

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Abstract—In situ-generated N-heterocyclic carbene (NHC) palladium catalysts and isolated NHC-palladium complexes have been tested for the telomerization reaction of 1,3-butadiene with primary and secondary amines. Superior catalyst activity (TON up to 400.000) and selectivity are obtained. Applying optimized conditions a variety of octa-2,7-dienylamines were prepared in high yield and excellent selectivity.

The palladium-catalyzed telomerization of 1,3-dienes with nucleophiles which was established independently by Smutny and Takahashi in 1967 is an ideal example for an environmentally benign synthetic method. Easily available starting materials are converted in the presence of a catalyst in a 100% atom efficient manner to give functionalized octa-2,7-dienes.[1–3] The resulting products have been used as intermediates in the total synthesis of several natural products,[4] as well as precursors for plasticizer alcohols,[5] industrial monomers, solvents, corrosion inhibitors, and non-volatile herbicides.[6]

In 2002, we described for the first time the use of palladium carbene complexes for telomerization reactions. Since then, we have demonstrated the superior catalyst productivity of these complexes for the telomerization of butadiene[7] and isoprene[8] with alcohols. Recently, we became also interested in similar reactions of amines. Many efforts have been made to investigate the telomerization of 1,3-butadiene with ammonia,[9] primary,[10] and secondary amines.[11] Most notably in 2003 Nolan and co-workers[12] applied cationic N-heterocyclic carbene (NHC) palladium complexes to convert 1,3-butadiene and different amines to the corresponding telomers. Unfortunately, to date all known telomerizations of amines require high catalyst loadings (>0.1 mol %), which makes these reactions less attractive for the preparation of bulk and fine chemicals. Here, we describe telomerization reactions of 1,3-butadiene with different primary and secondary amines with unexpectedly high catalyst activity. To the best of our knowledge the highest catalyst turnover number ever reported for this reaction is achieved.

Initially, molecular-defined (carbene)palladium(0) complexes were tested for the model reaction of piperidine with 1,3-butadiene (Scheme 1, Table 1).[13] In exploratory experiments we discovered that tetrahydrofuran and toluene are not suitable solvents for these reactions. Surprisingly, in the presence of methanol, a potentially competing nucleophile, as solvent the reaction is faster and proceeded selectively to give the N- and not the O-telomer! Therefore, in contrast to previous work high catalyst substrate ratios (1:100,000–200,000) were used in our studies.

All catalysts applied are shown in Figure 1. Even at very low catalyst concentration conversions up to 91% and excellent selectivity (99%) are observed with 1,3-di-mesitylimidazolin-2-ylidenepalladiumtetramethyldivinyldisiloxane **1** and the saturated 1,3-dimesityl-4,5-dihydroimidazolin-2-ylidenepalladiumtetramethyldivinyldisiloxane **2**. To our delight only the linear telomerization product is formed.

Keywords: Amines; 1,3-Butadiene; Carbene; Homogeneous catalysis; Palladium.
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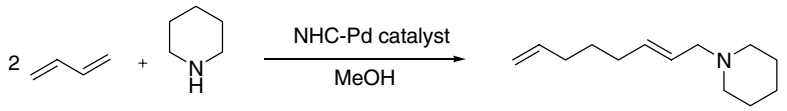


Scheme 1. Telomerization reaction of 1,3-butadiene with piperidine.

Table 1. Telomerization of 1,3-butadiene with piperidine in the presence of defined palladium catalysts

Entry	Catalyst	[Pd] (mol %)	Yield[a] (%)	Selectivity[b] (%)	TON[c]
1	**1**	0.001	91	99	182,000
2	**1**	0.0005	42	99	168,000
3*	**1**	0.0005	98	99	392,000
4	**2**	0.001	91	99	182,000
5	**3**	0.001	69	99	138,000
6	**4**	0.001	42	99	84,000
7	**4** + $NaBF_4$	0.001	47	99	94,000
8*	—	—	<1	—	—

General conditions: 5.5 g butadiene, 10 mL MeOH, 5.6 mL piperidine (1.12 equiv), $T = 90$ °C, $t = 20$ h, $pN_2 = 30$ bar, * +0.005 mol **5**.
[a] Yield of octa-2,7-dienylpiperidine.
[b] Selectivity toward octa-2,7-dienylpiperidine.
[c] Catalyst turnover numbers with respect to 1,3-butadiene.

At 0.0005 mol % catalyst loading the effect of extra added ligand was studied (Table 1, entries 2 and 3). Increasing the ligand concentration resulted in a higher yield, which clearly shows that the added ligand counteracts degradation during the reaction. For 1,3-dimesityl-4,5-dimethylimidazolin-2-ylidenepalladiumtetramethyldivinyldisiloxane **3**, the bulkier methyl groups in the backbone led to a reduced yield (Table 1, entry 5). By addition of ligand without any palladium source no conversion takes place (Table 1, entry 8).

Compared to the palladium dvds complexes **1**–**3** the allylpalladium(II) complex **4** as well as the cationic derivative showed a lower catalyst activity (Table 1, entries 6 and 7).

Notably, we were also able to characterize the highly active catalyst **2** for the first time by X-ray crystallography (Fig. 2). The palladium atom adopts a distorted trigonal-planar coordination geometry (CE1–Pd1–CE2 130.9, C1–Pd1–CE1 114.8, C1–Pd1–CE2 114.2; CE1, CE2–mid-points of the C=C bonds of the diolefin). The bond length of Pd1–C1 is 2.091(3) Å and is in the range found for other complexes of this type.[7c]

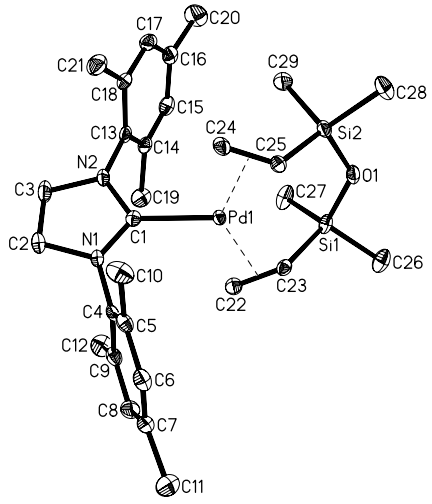


Figure 2. 1,3-Dimesityl-4,5-dihydroimidazol-2-ylidene Pd complex **2**.

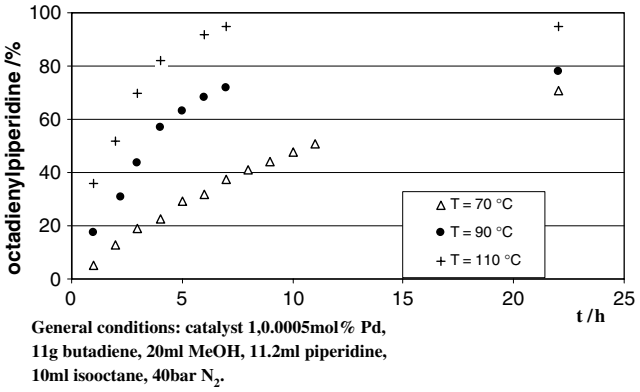


Figure 3. Catalyst activity at different temperatures.

As shown in Figure 3, **1** shows activity at 70 °C; however, at 110 °C the reaction is finished in 7 h with a yield of 95% octa-2,7-dienylpiperidine. Being able to take samples during the reaction these experiments were performed in a secured 160 mL stainless steel Parr

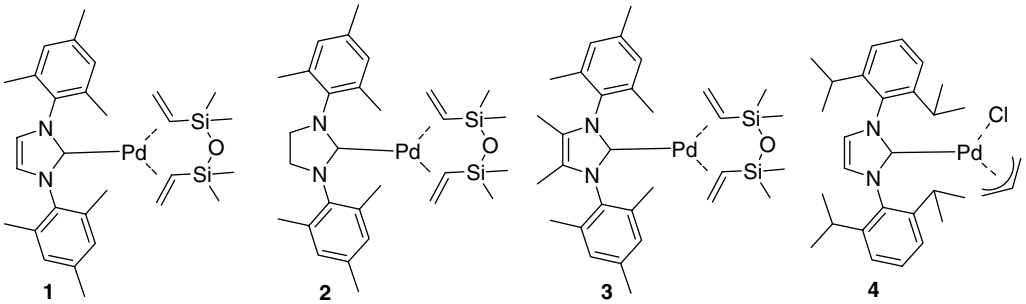


Figure 1. Tested catalysts for telomerization of 1,3-butadiene with piperidine.

autoclave with further changes in conditions. For this reason the yield at 90 °C (Table 1, entry 2) differs from the result shown in Figure 3.

Next, we compared the behavior of **1** with the corresponding in situ-generated Pd catalyst. Figure 4 clearly demonstrates the advantage of the in situ-system. Full conversion and quantitative yield of the desired product are obtained after 8 h at 90 °C. The lower yield in the presence of the isolated complex is explained by degradation of the ligand. Due to the improved catalyst productivity we compared different ligands for the in situ-generated catalysts in more detail. Table 2 shows selected results.

The palladium source and palladium-to-ligand ratio were chosen in agreement with our previous studies concerning the telomerization of alcohols.[7] As shown in Figure 5 imidazolium salts with different anion or imidazolium cations as well as imidazolin-2-ylidene:CO_2 adducts were tested.

In agreement with the defined complexes 1,3-dimesitylimidazolium salts gave better results compared to the 1,3-dimesityl-4,5-dimethylimidazolium and the 1,3-bis(2,6-diisopropylphenyl)imidazolium salts. Surprisingly the 1,3-dimesitylimidazolin-2-ylidene:CO_2 adduct **6** is the best catalyst (Table 2, entry 2). The nature of the anion can also have a significant influence. While

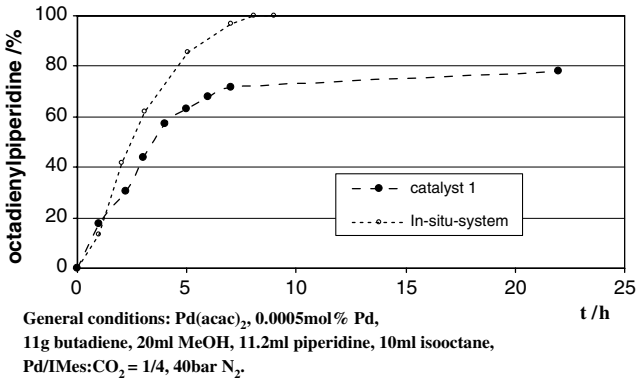


Figure 4. Comparison of the in situ versus preformed catalyst at 90 °C.

Table 2. Telomerization of 1,3-butadiene with piperidine in the presence of in situ-generated Pd catalysts

Entry	Ligand	Yield (%)	TON[a]
1	**5**	80	320,000
2	**6**	>99	400,000
3	**7**	54	216,000
4	PPh_3	61	244,000
5	PCy_3	52	208,000
6	**8**	49	196,000
7	**9**	56	224,000
8	**10**	84	336,000
9	**11**	10	40,000
10	**12**	3	12,000

General conditions: 5.5 g 1,3-butadiene, 10 mL MeOH, 5.6 mL piperidine (1.12 equiv), $T = 90$ °C, $t = 20$ h, $pN_2 = 30$ bar, Pd/Ligand = 1/4, [Pd] = 0.0005 mol %, ($Pd(acac)_2$).
[a] Catalyst turnover numbers based on 1,3-butadiene.

the mesylate and chloride (Table 2, entries 1 and 8) are comparable, a dramatic reduction in activity is seen for bromide and iodide anions (Table 2, entries 9 and 10). On the one hand, the formation of the ylidene species out of the 1,3-dimesitylimidazolium bromide and iodide may be hindered; on the other hand, the more nucleophilic anions may bind to the metal center

Table 3. Telomerization of 1,3-butadiene with secondary amines

Entry	Catalyst	Amine	Yield[a] (%)	Selectivity[b] (%)
1	**1**	Pyrrolidine	96	99
2	**5**/$Pd(acac)_2$		90	99
3	**1**	Morpholine	95	99
4	**5**/$Pd(acac)_2$		92	99
5	**1**	Dibenzylamine	81	99
6	**5**/$Pd(acac)_2$		78	99
7	**1**	Diethylamine	85	99
8	**5**/$Pd(acac)_2$		89	99
9	**1**	*N*-Methylaminoethanol	95	99
10	**5**/$Pd(acac)_2$		93	99
11	**1**	*N*-Phenylpiperazine	99	99
12	**5**/$Pd(acac)_2$		99	99

General conditions: 5.5 g butadiene, 10 mL MeOH, Pd = 0.005 mol %, $Pd(acac)_2$, 1.12 equiv amine, $T = 90$ °C, $t = 20$ h, $pN_2 = 30$ bar.
[a] Yield of octa-2,7-dienylamine.
[b] Selectivity toward linear octa-2,7-dienylamine.

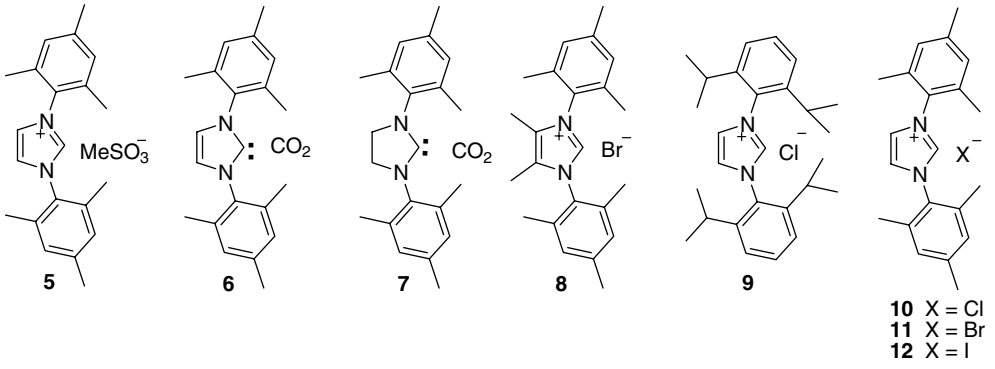
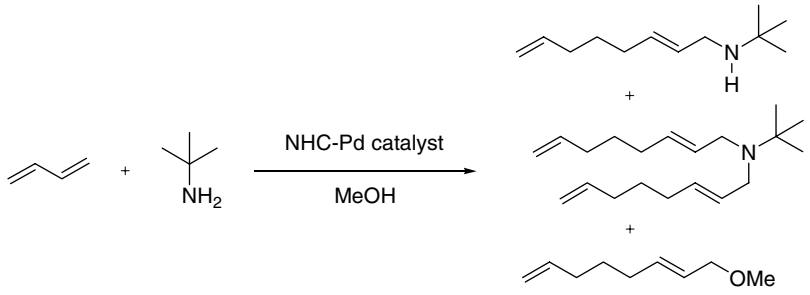


Figure 5. Ligands tested for the in situ catalysts.

Table 4. Telomerization of 1,3-butadiene with different primary amines in the presence of Pd carbene catalysts

Entry	Catalyst	amine	[Pd] (mol %)	mono-N-telomer[a] (%)	Di-N-telomer[b] (%)	O-telomer[c] (%)
1	**1**	Adamantylamine	0.005	22	<1	7
2	**5**/Pd(acac)$_2$		0.05	**63**	<1	37
3	**1**	*tert*-Butylamine	0.005	17	1	79
4*	**5**/Pd(acac)$_2$		0.05	**40**	12	0
5	**2**	Cyclohexylamine	0.005	9	<1	<1
6	**6**/Pd(acac)$_2$		0.05	**70**	15	15
7	**1**	*n*-Hexylamine	0.005	17	11	3
8	**5**/Pd(acac)$_2$		0.05	**55**	25	4

General conditions: 5.5 g butadiene, 10 mL MeOH, *10 ml MeCN, 1.12 equiv amine, Pd(acac)$_2$, $T = 90$ °C, $t = 20$ h, $pN_2 = 30$ bar.
[a] Yield of octa-2,7-dienylamine.
[b] Yield of bis(octa-2,7-dienyl)amine.
[c] Yield of methoxyocta-2,7-diene.



Scheme 2. Telomerization of *tert*-butylamine with 1,3-butadiene.

and thus produce poorly active catalysts. Notably, triphenylphosphine and tricyclohexylphosphine led to significant product yields in the range of 50–60 % (Table 2, entries 4 and 5). It should be mentioned that further reduction of the palladium amount is conceivable by using ligand **6** with a higher palladium/ligand ratio.

To determine the scope and limitation of the optimized catalyst system various secondary amines were reacted with 1,3-butadiene. As shown in Table 3 all educts are converted in high yield and excellent selectivity. There is no general trend whether the in situ or the preformed complex is more reactive. For example, complex **1** gave a 6% higher yield of the corresponding telomer with pyrrolidine, whereas the telomer of diethylamine is obtained in higher yield by the in situ catalyst. By testing different aliphatic, alicyclic, and benzylic amines we found that diethylamine and dibenzylamine are less reactive than the further tested amines. Notably, the reaction of *N*-methyl-2-aminoethanol gave selectively the N-telomer.

Finally, we applied different primary amines in the telomerization reaction (Table 4). It is well known that the reactivity of the telomerization of amines with 1,3-butadiene decreases in order secondary amine > primary amine > ammonia. In addition, double telomerization products can be formed in these reactions (Scheme 2).

At 0.005 mol % catalyst loading conversion of the primary amines to the corresponding telomers is low. Here, the major byproducts are the methoxytelomer and the bis(octa-2,7-dienyl)amines, which are formed for the less sterically hindered amines.

However, increasing the catalyst amount to 0.05 mol % led to sufficient yields. Adamantylamine, for example, gave 63% of the corresponding octadienylamine (Table 3, entry 1). Similar yields were obtained for cyclohexyl and *n*-hexylamine, while *tert*-butylamine gave a somewhat lower yield (Table 3, entries 4, 6, 8).

In conclusion, we have developed the first time highly efficient telomerizations of 1,3-butadiene and amines. By applying defined monocarbenepalladium(0)dvds complexes as well as in situ-generated catalysts unprecedented catalyst activity was obtained. The catalysts also show remarkable selectivity for a number of amine telomerization reactions. Further studies on amine telomerizations are currently underway in our laboratory.

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13. *General procedure for catalytic telomerizations*: One milliliter of a stock solution containing 1.24 mg of palladium acetylacetonate (5.1×10^{-7} mol) in 8 mL MeOH and 9 mL of a stock solution containing 1.42 mg of ligand**6** (2.0×10^{-6} mol) in 18 mL MeOH were added in a dried and sealed vessel under argon. Afterwards 5.6 mL piperidine (5.7×10^{-2} mol) was added. The mixture was transferred under argon into a secured 100 mL stainless steel Parr autoclave. The autoclave was cooled with dry ice and 5.5 g (1.01×10^{-1} mol) of 1,3-butadiene was condensed in a separate 75 mL pressure cylinder (mass control). The defined amount of 1,3-butadiene was condensed into the cooled autoclave and the vessel was heated to the desired reaction temperature. After 20 h the autoclave was cooled to room temperature and 5 mL of isooctane as internal standard was added. In general, the yield of telomers was determined by GC using HP 6869A gas chromatograph. The main products were isolated from the reaction mixture via distillation.