



Short communication

# First telomerisation of piperylene with morpholine using palladium-carbene catalysts



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## ABSTRACT

Telomerisation of common 1,3-dienes like butadiene and isoprene has already been successfully conducted with a huge number of nucleophiles. However, 1,3-pentadiene (piperylene) telomerisation with amines has not been reported yet. Here, we present the first telomerisation of piperylene with morpholine, providing an atom economic access to unsaturated C<sub>10</sub>-amines in a single reaction step. Investigations of the reaction conditions such as precursor and ligand screening led to Pd(acac)<sub>2</sub>/IMes·HCl being the most active catalyst.

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## 1. Introduction

Having in mind the diminishing resources of fossil feedstocks, one major goal of catalysis is the development of efficient synthesis routes based on either new feedstocks or on well-known, yet unutilized compounds. Among those is piperylene (1,3-pentadiene) **1** which is easily available from naphtha pyrolysis. It exhibits potential chemical properties; but so far it is usually hydrogenated to *n*-pentane and then isomerised to *iso*-pentane which is used as a gasoline additive [1]. One promising convenient access to long chained olefins offering a further functionality is the homogeneously catalysed telomerisation of 1,3-dienes [2].

The reaction has been independently developed by Takahashi [3] and Smutny [4] while investigating butadiene oligomerisation in the 1960s. Since the early days, there have been huge efforts in reacting 1,3-dienes with several functional groups such as alcohols [5–7], polyols [8–10], amines [11–13] and carbon dioxide [14,15]. By far the most used 1,3-diene is butadiene, which can be regarded as a standard model compound in telomerisation [16]. Up to now, it is the only 1,3-diene which made it to industrial stage, as it is used, for example, in the Kuraray process for the production of 1-octanol [17–19]. Dow in Tarragona uses butadiene in the production of 1-octene [20,21]. So far there are only few contributions of piperylene telomerisation dealing mainly

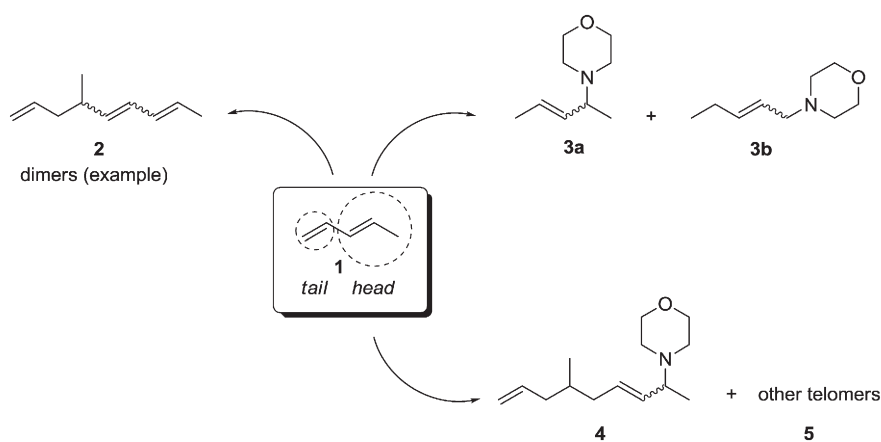
with oxygen nucleophiles [22–24]. Nevertheless, piperylene telomerisation has also been achieved with carbon dioxide [25], sulfones [26], and trimethylsilane [27]. To the best of our knowledge, there is no telomerisation of piperylene described with amines. For long time, telomerisation reactions have been catalysed by palladium/phosphine catalytic systems. However, in 2002 Beller et al. reported on the first catalytic system with a *N*-heterocyclic carbene ligand which is active in telomerisation [28].

## 2. Experimental

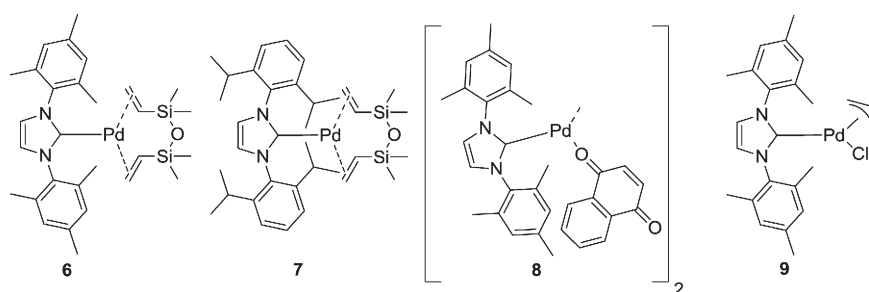
All screening experiments were performed in a 10 ml homemade multiplex reactor, while TMS Systems were conducted in a 20 ml homemade steel reactor [41]. In a typical experiment, the precursor (0.045 mmol) was dissolved in 6 ml methanol. After the addition of piperylene (1156 mg, 15 mmol) and morpholine (1476 mg, 17 mmol), the resulting mixture was transferred to the evacuated and flame dried reactor. The reactor was charged with 5 bar argon to prevent the mixture from oxygen as well as moisture contact and placed in an oil bath at the reaction temperature. The stirrer was set to 500 rpm. After 16 h at reaction temperature the reactor was placed in an ice bath and allowed to come to room temperature. The reactor was depressurised and a sample was analysed by gas chromatography with di-*n*-butylether as an internal standard and toluene as an additional solvent. The hydroamination products **3a** and **3b** as well as the main telomerisation product **4** were isolated and characterized by <sup>1</sup>H- and <sup>13</sup>C

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**Scheme 1.** Different possible reaction routes in telomerisation of piperylene with morpholine.



**Fig. 1.** Structures of selected palladium carbene precursors.

NMR spectroscopy (see Supplement). The carbene precursors used in this contribution have been synthesised by known methods [30–32].

### 3. Results and discussion

1,3-Pentadiene is an unsymmetrical diene, which leads to several possible products: the internal double bond of piperylene is referred to as “head” in telomerisation, while the terminal double bond is referred to as “tail”. An overview on possible linkages can be found in a review on piperylene functionalisation, which we have published, recently [1].

Although, the telomerisation is known to be a very selective reaction, there are some typical side products, which occur under feasible conditions (Scheme 1).

A typical side-reaction covers the formation of piperylene dimers, for instance (2), which are identified by GC–MS, with no further structure determination. Another typical side reaction involves formation of 1:1 adducts between piperylene and morpholine, which are formed in a hydroamination (HA) reaction (3). The main product during

piperylene telomerisation has been determined to be the tail/head (*t/h*) product 4. During our investigations, there occurred also small amounts of other telomers, which were determined by GC–MS coupling. In the following experiments, these will be counted as (5).

Initial investigations were focussed on screening different palladium precursors which comprise one or two carbene ligands (Fig. 1).

We started our investigations with a piperylene/amine ratio of 2:2.25 to avoid a lack of morpholine during the reaction. The reactions have been conducted in methanol (MeOH), as it is reported to be a suitable solvent in telomerisation with amines without competing as a nucleophile [33]. All primary screening experiments were carried out in a 10 ml multiplex reactor developed by our workgroup [29]. The results are shown in Table 1.

When precursor 6 is used at different concentrations (entries 1/1 to 1/3), it turned out that higher loadings of about 0.3 mol% are required in contrast to telomerisation of butadiene or isoprene which are also active at lower concentrations. This catalyst concentration has been chosen for screening several other precursors; however, 6 afforded the highest overall telomer yields of 35% with a selectivity of 90%. In contrast, the structurally similar precursor 7 tends to give a slightly higher yield of

**Table 1**  
Primary screening of palladium precursors.

Entry	Precursor	mol%	Conversion of piperylene [%]	Y(2) [%]	Y(3) [%]	Y(4) [%]	Y(5) [%]	S(4) [%]
1/1	6	0.1	6	2	1	1	2	17
1/2	6	0.2	5	2	0	0	3	0
1/3	6	0.3	37	1	1	33	2	90
1/4	7	0.3	25	11	0	11	3	44
1/5	8	0.3	14	0	0	11	3	78
1/6	9	0.3	12	10	0	1	1	8

Conditions:  $n_{\text{piperylene}} = 15 \text{ mmol}$ ,  $n_{\text{Morpholine}} = 17 \text{ mmol}$ ,  $t = 16 \text{ h}$ ,  $T = 100 \text{ }^\circ\text{C}$ , 6 ml MeOH, 500 rpm, 5 bar argon, Y = yield, S = selectivity.

**Table 2**  
Influence of the solvent.

Entry	Solvent	Conversion of piperylene [%]	Y(2) [%]	Y(3) [%]	Y(4) [%]	Y(5) [%]	S(4) [%]
2/1	Methanol	36	1	1	30	4	83
2/2	Dioxane	27	20	0	6	1	22
2/3	Dimethylformamide	24	0	1	19	4	79
2/4	Isopropanol	16	9	0	3	4	19
2/5	Acetonitrile	5	5	0	0	0	0

Conditions: 0.3 mol% 6,  $t = 16 \text{ h}$ ,  $n_{\text{piperylene}} = 15 \text{ mmol}$ ,  $n_{\text{Morpholine}} = 17$ ,  $t = 16 \text{ h}$ ,  $T = 100 \text{ }^\circ\text{C}$ , 6 ml solvent, 500 rpm, 5 bar argon.

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