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Priority Communication

One-step palladium catalysed synthetic route to unsaturated pelargonic C_9-amides directly from 1,3-butadiene

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ABSTRACT

The first example of the palladium catalysed *amidotelomerisation* is presented, in style of the ambitious carboxytelomerisation. A straightforward synthetic tool was generated to produce several industrial relevant pelargonic C_9-amides based on the fundamental chemical feedstocks: 1,3-butadiene, carbon monoxide and secondary amines. The reaction network was uncovered and crucial influences were determined by *design of experiments (DoE)*. Through the incorporation of an *auto*-tandem palladium acetate/diphenylphosphino ethane catalytic system, very good yields up to 77% of the desired amides and excellent selectivities of carbonylation products of 94% were achieved. The application of the amidotelomerisation conditions to different classes of amines offered a broad range of the corresponding pelargonic C_9-amides. Understanding the tandem catalysis, significant inhibition factors were uncovered and through a stepwise optimisation, for the first time a carbonylation reaction of octadienyl amines (telomer products) was shown, yielding in 99% of the desired linear pelargonic C_9-amide.

1. Introduction

In the last years, the development of environmentally friendly synthesis tools for the preparation of organic amides moved into the focus of academia and industry. Particularly, complex organic multi-step amide synthesis concepts with high E-factors are going to be replaced by straightforward transition metal catalysed carbonylation reactions [1–5].

In this context, the homogeneous palladium catalysis offers the utilisation of a broad range of different substrates to amides [6]. For instance, 1,3-dienes [7], allylic alcohols [8] or amines [9–12] and olefins [13] can be converted to amides by applying transition metal carbonylation catalysts.

Generally, the class of amides is representative for high-value compounds with a strong relevance for industrial applications in agriculture and medicine [2]. To mention important examples, the pelargonic C_9-amides and its derivatives are compounds with a versatile application, *e.g.* as herbicides, rabbit repellents and capsaicin analogues [14].

One 100% atom economic palladium catalysed carbonylation reaction, which gives access to the synthesis of the pelargonic esters and its derivatives, is the carboxytelomerisation [15,16]. Very recently, we have shown that the carboxytelomerisation is an elegant synthesis method to convert 1,3-butadiene, carbon monoxide and methanol to the unsaturated C_9-pelargonic acid ester (Scheme 1). By applying palladium acetate and tri-*n*-butyl phosphine as ligand in pyridine, excellent reaction performances were achieved, quantitatively yielding the desired ester in 99% selectivity [17].

2. Results and Discussion

In the present work, for the first time we establish the palladium catalysed *amidotelomerisation* of 1,3-butadiene, carbon monoxide and amines. The target products, the pelargonic C_9-amides are synthesised directly from fundamental chemical feedstocks. To the best of our knowledge, this is the first example of a linkage of an amine telomerisation with a carbonylation reaction to provide the direct formation of the desired C_9-amides in a one-pot synthesis. Unfortunately, the simple transfer of the carboxytelomerisation reaction conditions is not expedient. The investigation of different ligands led to a broadened product spectrum in comparison to the conversion of alcohols to C_9-esters with low yields of the desired pelargonic C_9-amides. In Scheme 2, all competing palladium catalysed amination and carbonylation reactions are illustrated in the resulting reaction network.

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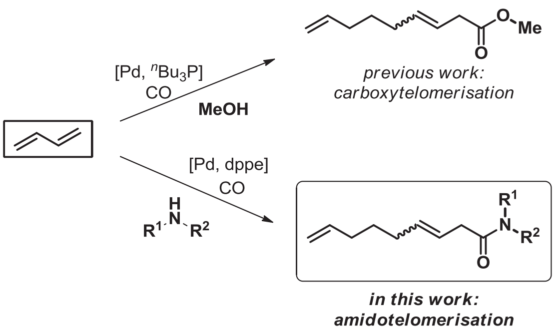
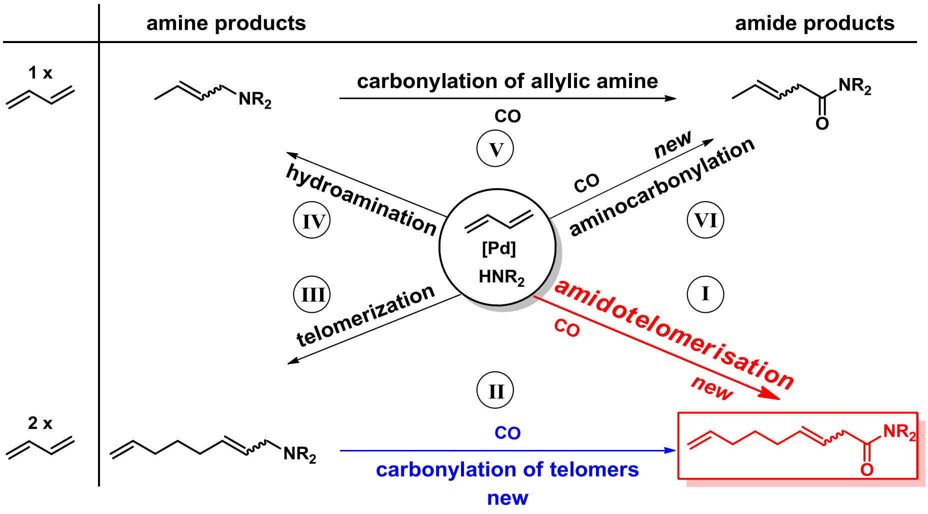


Scheme 1. Depiction of the carboxytelomerisation and the new *amidotelomerisation* presented in the present work.

The reaction network was uncovered based on the palladium acetate catalyst in combination with diphenylphosphino propane (dppp) as an example of a bidentate ligand, which is known for high reaction rates in carbonylation reactions of allylic compounds [18]. In general, a reaction network comprising hydroamination, telomerisation and carbonylation reactions of the resulting allyl amines was observed. More precisely, the proposed *amidotelomerisation* **I** as well as the amine telomerisation **III** or rather the carbonylation of the telomers **II** can occur yielding all in the desired C_9-amide by conversion of two mole 1,3-butadiene. On the other hand, by utilisation of one mole 1,3-butadiene, the hydroamination **IV**, carbonylation of the hydroamination product **V** and the combination, the direct aminocarbonylation **VI** can be observed all providing the formation of the C_5-amide. To the best of our knowledge, the aminocarbonylation of 1,3-butadiene to the C_5-amide **VI**, the carbonylation of the telomer **II** and the proposed *amidotelomerisation* **I** is not reported in literature to date.

Based on the successful application of dppp as ligand, a software supported *design of experiments (DoE)* was created to determine and validate crucial reaction parameters. The following significant trends were defined for selected ranges of crucial factors (for detailed information see the Supporting material):

- Low phosphine to palladium ratio leads to higher yields of the desired C_9-amide
- The higher the 1,3-butadiene to amine ratio, the higher the yields of the desired C_9-amide



Scheme 2. Competing reaction network under amidotelomerisation reaction conditions.

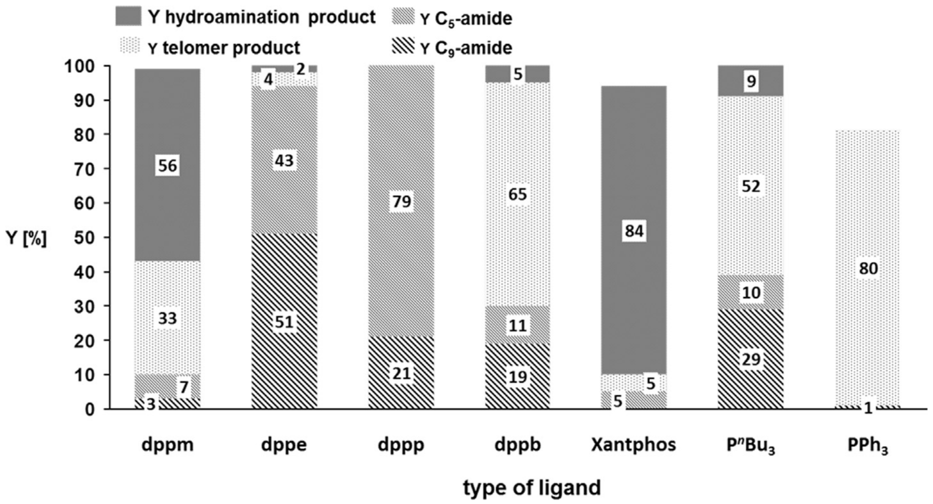


Fig. 1. Influence of the ligand in the palladium catalysed amidotelomerisation. Reaction conditions: 1.85 mmol diethyl amine, 9.24 mmol 1,3-butadiene (5 eq.), 5 mol% Pd $(OAc)_2$, Pd:ligand = 1:2, 2 mL toluene, p = 20 bar CO, T = 110 °C, t = 18 h; X = conversion, Y = yield; dppm = diphenylphosphino methane, dppe = diphenylphosphino ethane, dppp = diphenylphosphino propane, dppp = diphenylphosphino butane, Xantphos = 4,5-bis(diphenylphosphino)-9,9-methyl xanthene, P^nBu_3 = tri-*n*-butyl phosphine, PPh_3 = triphenyl phosphine; all results determined *via* GC-FID-analysis.