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Letter

Effects of chelating diphosphines on the rhodium catalysed carbonylation of allylamines

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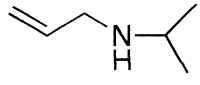
Carbonylation of allylamine catalysed by rhodium/phosphines systems produces γ-lactams in good yields [1–3]. Lactams are very important compounds as starting material for the synthesis of anti-inflammatory and antibiotic drugs [4,5]. Recently, we found that mono-phosphorated ligands such as PPh_3 form much more reactive systems with rhodium than the biphosphorated ones [6]. Usually, the diphosphine ligands lead to almost no conversion of the allylamines used as substrates. Chelating phosphines have been extensively studied mainly for hydroformylation of olefins catalysed by rhodium complexes [7]. The chelation angle (*bite angle*) of these ligands has been pointed out as the principal factor affecting the normal/iso ratio for the produced aldehydes [8,9]. However, the most important use of diphosphines is as a chirality inductor ligand in catalytic asymmetric syntheses. This work presents the first systematic studies on catalytic carbonylation of allylamines by rhodium-diphosphine systems, evaluating both the effects of the chelating angle, formed between the metal and the phosphorous atoms, and of the alkyl group attached to the nitrogen atom, on the nature and selectivity of the products.

The catalytic systems were prepared in situ, mixing $RhCl_3 \cdot 3H_2O$ and equimolar amounts of the diphosphine ligands (1,2-diphos (1,2-bis(diphenylphosphino)etane); 1,3-diphos (1,3-bis(diphenylphosphino)propane); 1,4-diphos (1,4-bis(diphenylphosphino)butane)) or four-fold excess of monophosphorated ligands (triphenylphophine and triphenylphosphite) in THF (dried over Na/benzophenone and distilled under argon). Two substrates were studied: isopropylallylamine and *n*-butylallylamine. These allylamines were prepared as reported in the literature with minor modifications [10].



isopropylallylamine

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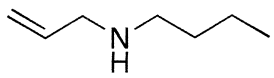


n-butylallylamine

The reactions were carried out into a stainless steel Teflon lined autoclave. The samples were quantified by gas chromatography using cyclooctane as internal standard. The reaction products were identified through GC/MS by comparison with authentic samples [1]. Lactam was also characterized by its ^{1}H NMR spectrum.

Four-fold excess of PPh_3 and $P(OPh)_3$ was used to insure the formation of $RhCl(CO)(PR_3)_2$ precursor species [11]. This approach was validated by the very close values of conversion and selectivity observed in the reactions started by either $RhCl(CO)(PPh_3)_2$ or $RhCl_3 \cdot 3H_2O/PPh_3$ (Tables 1 and 2). In the case of diphosphines, equimolar amounts related to the rhodium were required, because it was previously shown that the use of two-fold excess ([P]/[Rh] = 4) produces almost inactive catalytic systems [12]. This result was ascribed to the formation of stable phosphine chelated species.

So, either in the monophosphine or in the diphosphine experiments the precursor species would be $RhCl(CO)(P)_2$, ([P]/[Rh] = 2).

Scheme 1 presents the products of the isopropylallylamine carbonylation, arranged in accordance to their chromatographic retention times. Their distribution as a function of the catalytic system are shown in Table 1.

All the systems tested showed high conversions but the selectivity decreased as the diphosphine carbon chain increased. The main products in all cases were: isopropylamine, **1a**, resulting of the catalytic substrate deallylation [13–16]; an isomerization product, **1b**; pyrrolidine, **1c** and pyrroline, **1d**. Fig. 1 shows that up to 9 h, the two main products in the reaction mixture were lactam **1g** and pyrroline **1d**, with pyrrolidine **1c** as a minor product. From 9 h up to the end of the reaction time, the lactam concentration remained almost constant; the pyrroline content decreased while the pyrrolidine increased. This kinetic study suggests that: (i) the lactam was not a source to the pyrroline or pyrrolidine; (ii) the pyrrolidine was produced from the pyrroline hydrogenation. The most reasonable route to the pyrroline **1d** production seems to be a hydroformylation/dehydration of the substrate. Scheme 2 (R = isopropyl) presents the proposed steps for the formation of pyrroline and pyrrolidine.

The best yields of the desired product, *N*-isopropyl-butyrolactam **1g**, was obtained for the PPh_3-based systems. The mechanism for the lactam formation is shown Scheme 3 (R = isopropyl) [6].

In the presence of $P(OPh)_3$, isomerization was the main reaction. This change in selectivity is certainly due to the higher σ-acidity of the phosphites compared to the phosphines.

The minor products, **1e**, **1f** and **1h** (3% to 8%), were observed only in the presence of 1,4-diphos. [2] Their structures were proposed on the basis of their mass fragmentation. Product **1e** presents a very small molecular peak; $m/e = 113$, abundance = 10% and the main peak at $m/e = 98$, is related to a methyl loss. This fragmentation is typical of a linear product. On the other hand, products **1f** and **1h** show very intense molecular peaks: $m/e = 123$, abundance = 55% and $m/e = 151$, abundance = 50%, respectively, characteristic of stable cyclic structures. The main peak in the **1f** mass spectrum occurs at $m/e = 80$, derived from an iso-

[1] The mass spectra of the products **1a**–**1h** and **2a**–**2h** are available as supplementary material from the author.

[2] **1e** would be formed by the hydroformylation of the substrate, followed by hydrogenation of the aldehyde carbonyl and dehydration of the resulting amino-alcohol. Thus, the formation mechanism of **1e** and **1d** would be closely related (Scheme 2) with the cyclization step missing in the case of **1e**.

Table 1
Isopropylallylamine carbonylation

Catalytic system	[P]/[Rh]	Conversion (%)	Products (%)							
			1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
$PPh_3/RhCl_3 \cdot 3H_2O$	4/1	79.5	30.6	–	12.7	–	–	–	56.7	–
$RhCl(CO)(PPh_3)_2$	–	100	–	8.3	25.6	7.5	–	–	58.7	–
$P(OPh)_3/RhCl_3 \cdot 3H_2O$	4/1	84.4		55.9		–	–	–	44.1	–
1,2-Diphos/$RhCl_3 \cdot 3H_2O$	2/1	100		20.0	40.6	–	–	–	39.4	–
1,3-Diphos/$RhCl_3 \cdot 3H_2O$	2/1	97.4	12.3	20.0	43.4	–	–	–	24.3	–
1,4-Diphos/$RhCl_3 \cdot 3H_2O$	2/1	100	12.0	9.7	19.9	31.0	5.5	4.3	9.3	8.3

Reaction conditions: 0.038 mmol [Rh], 752 mg (7.6 mmol) of isopropylallylamine, 500 mg cyclooctane (internal standard), 30 ml of THF, CO/H_2 (20 bar, 4/1), 70°C, 300 rpm, 24 h.

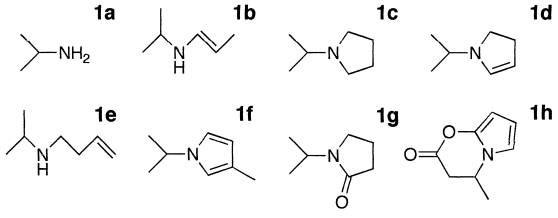
Table 2
n-Butylallylamine carbonylation[a]

Catalytic system	[P]/[Rh]	Conversion (%)	Products (%)							
			2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
$PPh_3RhCl_3 \cdot 3H_2O$[b]	4/1	100	4.0	–	11.4	–	–	–	73.6	–
$RhCl(CO)(PPh_3)_2$	–	100	8.3	–	11.5	6.0	–	2.2	72.0	–
$P(OPh)_3/RhCl_3 \cdot 3H_2O$	4/1	52.0	–	23.6	–	6.7	13.3	10.6	45.8	–
1,2-Diphos/$RhCl_3 \cdot 3H_2O$	2/1	25.0	–	–	–	–	100	–	–	–
1,3-Diphos/$RhCl_3 \cdot 3H_2O$	2/1	26.0	–	–	–	–	100	–	–	–
1,4-Diphos/$RhCl_3 \cdot 3H_2O$[c]	2/1	100	14.1	–	11.5	23.5	–	–	36.6	7.8

[a] 859 mg (7.6 mmol) of *n*-butylallylamine.
Reaction conditions as in Table 1.
[b] 11% Heavy products.
[c] 6.5% Heavy products.

propyl ($m/e = 43$) loss. The stability of this fragment is also an evidence of the cyclic nature of that product. In the case of product **1h**, the main peak is observed at $m/e = 136$, arising from a methyl loss. The stability of this cation radical could be explained by the electronic delocalization allowed by its molecular structure.

Possible mechanisms for their formation will be discussed in a full paper. Even though, some



Scheme 1.

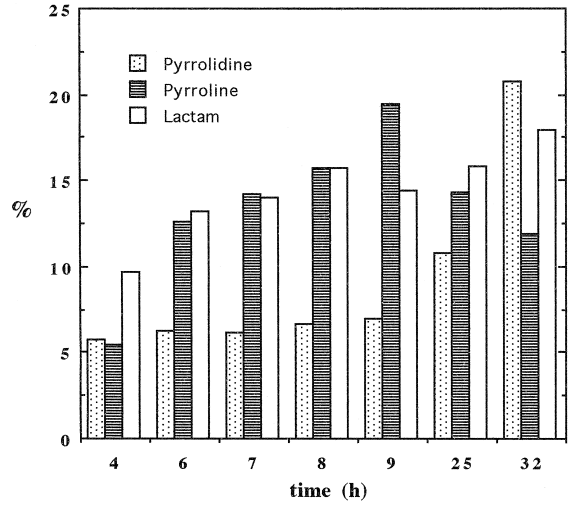
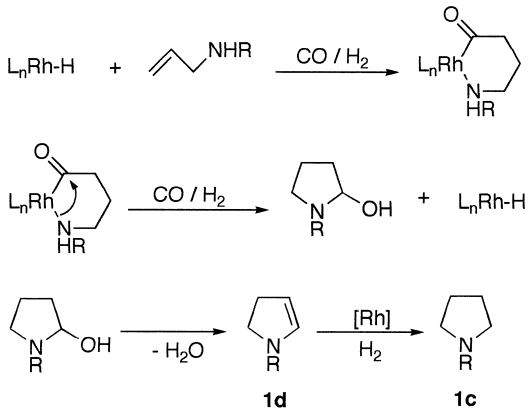


Fig. 1. Variation of the catalytic mixture composition as a function of time, during the carbonylation of isopropylallylamine catalysed by $RhCl_3 \cdot 3H_2O$/1,4-diphos under reaction conditions as stated on Table 1.



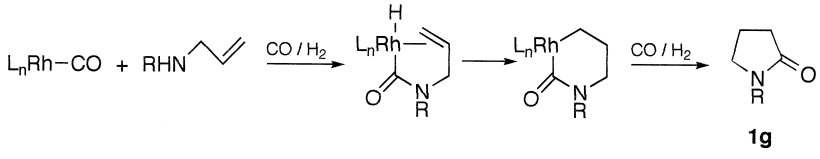
Scheme 2.

considerations about the presence of aromatic structures in products **1f** and **1h** should be made. It is clear that a dehydrogenation step is involved in their formation which, even under hydrogen pressure, could be explained taking into account that rhodium complexes are known to promote both hydrogen transfer and dehydrogenation [17,18]. Moreover, the hydrogen composition in the gas mixture is only 20% and its solubility is very low in almost all solvents.

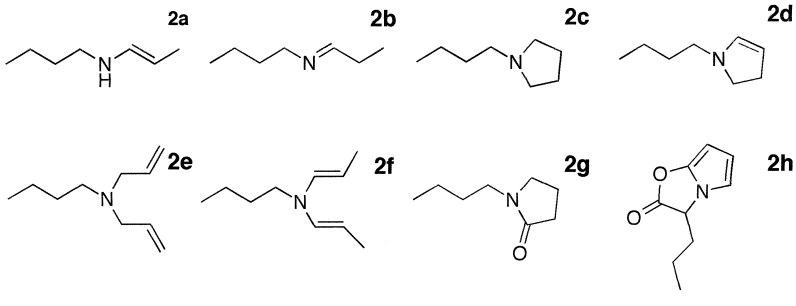
In order to evaluate the influence of the alkyl groups bound to the nitrogen on the selectivity to the corresponding lactam, the catalytic carbonylation of *n*-butylallylamine was also studied in the same reaction conditions (Table 2). The proposed products are depicted in Scheme 4.

As observed in the experiments with isopropylallylamine, PPh_3-based systems gave the best yields in lactam (**2g**) and $P(OPh)_3$ led to substrate isomerization as the main reaction. For 1,2-diphos and 1,3-diphos, conversions decreased drastically and the selectivity was driven to an unusual product (**2e**), formed by acatalytic disproportionation of the substrate. This behaviour might be ascribed to the restricted bite angle that these chelating phosphines can form with rhodium (90°–120°). The more flexible 1,4-diphos was able to convert the substrate completely with a reasonable selectivity to lactam. The product **2h** (analogue to **1h**, Scheme 1) was produced exclusively in the presence of 1,4-diphos. The mass spectrum of this product, as observed in the case of **1h**, presents a stable molecular ion; $m/e = 165$, abundance = 65% and the main peak at $m/e = 122$, generated by an *n*-propyl ($m/e = 43$) loss.

In conclusion, the results obtained in the rhodium catalysed carbonylation of allylamines using diphosphines showed a remarkable influence of the bite angle in both conversion and selectivity ratios. The steric hindrance of the groups attached to the allylamines nitrogen atom



Scheme 3.



Scheme 4.

is determinant of the reaction results. It turned out that hydroformylation, isomerization, hydrogenation, deallylation, dehydrogenation and disproportionation may also take place in competition with the carbonylation reaction. These studies also served as the basis to further works in the asymmetric catalytic carbonylation of allylamines using chiral diphosphines.

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