

Rhodium-Mediated 100% Regioselective Oxidative Hydroamination of α -Olefins.

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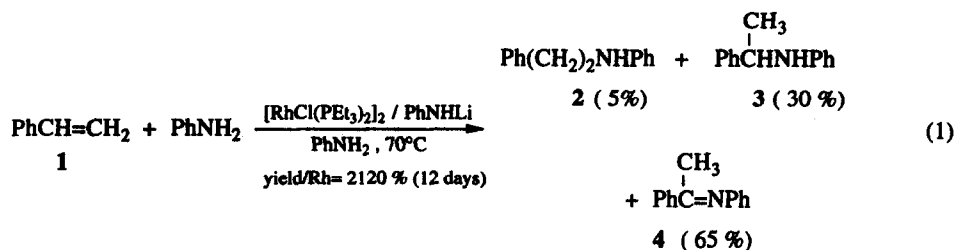
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Abstract : The system generated from lithium anilide and $[(Et_3P)_2RhCl]_2$ catalyzes (turnover 21) the regioselective condensation of aniline with styrene to give a mixture of $PhNH-CH(CH_3)Ph$ (hydroamination product) and $PhN=C(CH_3)Ph$ (oxidative hydroamination product) in *c.a.* 1/2 ratio. This 100% regioselective oxidative hydroamination has been confirmed in the case of 1-hexene.

The functionalization of α -olefins is a transformation of high synthetic interest.¹ Some of the most useful reactions, which are generally catalyzed by a transition metal derivative, result in the addition of an hydrogen atom and a Z functional group across the carbon-carbon double bond.² This apparently simple, direct addition process, however, fails in some cases. For instance, the hydroamination of olefins has not yet found satisfying applications in spite of its recognised potential interest for the industrial scale production of amines.³ A related, but less common process is the oxidative functionalization of olefins. Examples of such reactions are the oxidative carbonylation of ethylene to acrylic acid,⁴ and the oxidative hydration of ethylene to acetaldehyde (Wacker process).⁵

In the course of continuing studies directed toward the catalyzed hydroamination of alkenes,⁶ we have found a novel rhodium-catalyzed 100% regioselective oxidative hydroamination of styrene.

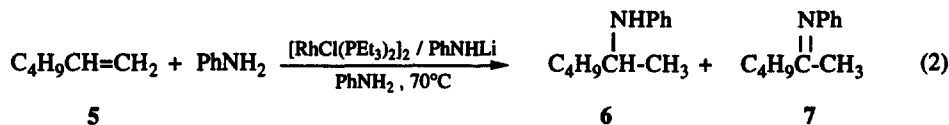
Styrene (**1**) (55 mmol) was added at room temperature to a system generated from *in situ* (-10°C) prepared lithium anilide (5 mmol) and $[(Et_3P)_2RhCl]_2$ ⁷ (0.5 mmol) in aniline (15 mL, \approx 165 mmol). The reaction mixture was then heated to 70°C. GC and GC-MS monitoring indicated the slow formation of three products, namely two amines (**2** and **3**) and a Schiff base (**4**), the latter being the major product (eq. 1). These were identified by comparison (GC retention times and mass spectra) with authentic samples prepared by conventional procedures.^{8,9} No trace of the corresponding linear chain imine ($PhCH_2CH=NPh$) could be detected. As a confirmation, GC analysis of the reaction mixture after hydrolysis indicated the formation of acetophenone and the absence of phenylacetaldehyde.



The formation of **3** and **4** was found to be reproducible and their relative ratio remained constant throughout the reaction. In contrast, the formation of **2** was less reproducible. Although the overall reaction proved to be slow, no deactivation of the system was observed for 12 days (turnover : 21). Moreover, it is catalytic with respect to both rhodium and lithium.

Control experiments indicated that no reaction occurs in the absence of lithium anilide. Furthermore, experiments conducted without the rhodium precursor resulted in a very slow, poorly reproducible reaction leading exclusively to the linear chain amine **2**.¹⁰ On the basis of these results, it can be proposed that the little amount of **2** formed in reaction (1) comes from the direct reaction of PhNHLi with styrene. It can thus be inferred that the rhodium-catalyzed condensation of aniline on styrene is 100% regioselective.

When a similar reaction was performed with 1-hexene, **5**, the same qualitative result was obtained. Two compounds were formed, namely an amine, **6**, and a branched chain imine, **7**, (15/85 ratio) both resulting from a selective condensation on the β carbon atom of 1-hexene (eq 2).



Compounds **6** and **7** were identified by comparison of their GC retention times and mass spectra with those of authentic samples prepared by classical procedures.^{8,9} No trace of either the linear chain amine (*N-n*-hexylaniline) or the imine (*N-n*-hexylideneaniline) could be detected (GC analysis). This latter observation confirms our hypothesis (*vide supra*) that, in the case of styrene, formation of the linear chain amine **2** is not rhodium-mediated.

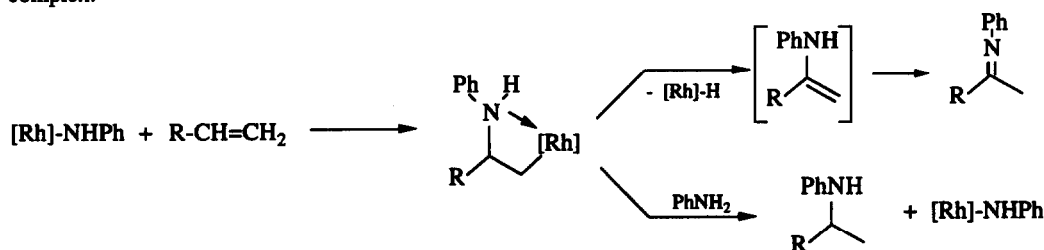
Although no quantitative data are available for the reaction of aniline with 1-hexene, these results confirm both the regioselectivity of the reaction and the formation of oxidative hydroamination products.

The stoichiometric, low yield formation of imines has been previously observed in the reaction of *n*-butylamine with the ethylene Pd(II) chloride complex $[\text{PdCl}_2(\text{C}_2\text{H}_4)]_2$.¹¹ This reaction involves a β -

aminoethylpalladium(II) derivative "ClPdCH₂CH₂NH*n*-Bu" which decomposes in a manner similar to that by which the intermediate hydroxyethylpalladium (II) complex of the Wacker process gives acetaldehyde. The reaction, however, is not regioselective since, in the case of propene, a mixture of the two possible imines, Me₂C=N-*n*-Bu and MeCH₂CH=N-*n*-Bu has been obtained (6/1 ratio).¹¹ Moreover, to the best of our knowledge, no catalytic version of these reactions has been reported.

Thus, the observed rhodium-catalyzed, fully regioselective formation of imines appears unprecedented. The nature of the rhodium complex generated by reaction of LiNHPPh with [(Et₃P)₂RhCl]₂ has been investigated in THF. The ³¹P {¹H}NMR spectrum (Bruker AC 80, 32.438 MHz) of the resulting homogeneous solution exhibits a unique doublet at 38 ppm (*J*(P-Rh) = 171 Hz). On the basis of thorough NMR studies (including 2D (δ, δ) ³¹P, ¹⁰³Rh{¹H} NMR experiments) of similar reactions conducted with [(Ph₃P)₂RhCl]₂,¹² the above reaction is believed to generate an anionic bis(triethylphosphine)bis(anilido)rhodium species [(Et₃P)₂Rh(NHPPh)₂]⁻, Li⁺.

Although the reaction mechanism has not yet been investigated, it is proposed to involve (scheme) a fully regioselective insertion of the carbon-carbon double bond of the olefin into the Rh-N bond of an anilidorhodium complex.¹³



Decomposition (β-elimination) of the resulting 2-phenylaminoalkylrhodium species would lead to an enamine which, either within the coordination sphere or not, rapidly isomerizes to the corresponding imine. Regeneration of the anilidorhodium active species would then occur by reaction of the rhodium hydride with aniline, a reaction which is reminiscent to the reaction of tris(triphenylphosphine)rhodium hydride with phenol to give tris(triphenylphosphine)phenoxyrhodium.¹⁴

Work is in progress to determine the scope and limitations of this new catalytic functionalization of α-olefins and to gain more insight into the reaction mechanism.

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- 7) Prepared by reaction of triethylphosphine (4 equiv.) with $[(C_8H_{14})_2RhCl]_2$ in dichloromethane. $^{31}P\{^1H\}$ NMR (32.438 MHz)(THF), δ (ppm)(external reference: $H_3PO_4-D_2O$) : 41.2 (d, $J(P-Rh) = 193.4$ Hz).
- 8) Authentic samples of the amines were prepared by the reductive alkylation of aniline with the corresponding carbonyl compound (phenylacetaldehyde, acetophenone, hexanal, 2-hexanone) in the presence of $KHFe(CO)_4$ (Boldrini, G. P.; Panunzio, M.; Umani-Ronchi, A. *Synthesis* **1974**, 733)
- 9) Authentic samples of the Schiff bases were prepared from aniline and the corresponding carbonyl compound (phenylacetaldehyde, acetophenone, hexanal, 2-hexanone) by the classical method (Gilman, H.; Blatt, A. H., *Organic Syntheses* Coll. Vol. 1, 2nd Ed., J. Wiley & Sons, 1941). Prolonged reaction times and heating were necessary to obtain reasonable yields.
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- 13) A similar regioselective insertion of a carbon-carbon double bond into a Ln-N bond has recently been observed in the organolanthanide-centered hydroamination-cyclization of aminoolefins (Gagné, M.; Nolan, S. P.; Marks, T. J., *Organometallics* **1990**, *9*, 1716-1718)
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