Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 358 (2005) 2749–2754

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Addition of secondary amines to activated alkenes promoted by Pd(II) complexes: Use of ammonium salts as cocatalysts

Alessandro Del Zotto *, Walter Baratta, Alessandro Felluga, Pierluigi Rigo

Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Via Cotonificio 108, 33100 Udine, Italy

Received 24 December 2004; accepted 14 March 2005
Available online 7 April 2005

Abstract

The complexes [Pd(acac)$_2$] **1**, [Pd(hfa)$_2$] **2** (hfa = hexafluoroacetylacetonate), [Pd(CF$_3$CO$_2$)$_2$] **3** and [Pd$_3$(CH$_3$CO$_2$)$_6$] **4** exhibit very different catalytic efficiency in the reaction between secondary amines and activated alkenes. Complexes **1** and **4** generally show an enhanced activity when catalytic amounts of NH$_4$X salts (X$^-$ = low-coordinating anion) are added to the reaction mixtures. On the contrary, the activity of the perfluorurate analogues **2** and **3**, which is much higher than that of **1** and **4**, is generally scarcely affected by the presence of the NH$_4$X additive. The cocatalytic effect of NH$_4$X is comparable with that of strong acids such as CF$_3$SO$_3$H. The ammonium salts alone can behave as a catalyst giving an almost quantitative yield of the hydroamination product.

Keywords: Homogeneous catalysis; Palladium; Hydroamination; Amines; Alkenes

1. Introduction

The hydroamination of alkenes, i.e., the direct addition of amines or related compounds to the C=C bond, has received renewed attention in the last few years [1]. The hydroamination reaction constitutes an attractive, 100% atom-economic process of formation of amines from generally cheap and readily available starting materials without generation of waste products. Although various transition metal complexes have been shown to promote the hydroamination process, those of Ni(II) and Pd(II) are considered to be the most promising on the basis of DFT studies [2]. Effectively, a lot of work has been done using Pd(II)-based catalysts [3–14] and, among these, species bearing chiral ligands have been successfully employed in enantioselective syntheses [1b,4,8,10–13]. In the generally accepted reaction mechanism, the alkene is activated by coordination to the metal centre and the C–N bond is then generated by a nucleophilic attack of the amine on the coordinated alkene. Finally, the metal–C bond of the resulting ammonioalkyl complex has to be cleaved to release the product. The last one is considered to be the rate-determining step of the whole process and most of the investigations in this field have been directed towards the development of efficient cocatalysts able to promote the metal–carbon cleavage. In this context, it has been found that catalytic amounts of strong acids, such as CF$_3$SO$_3$H and CF$_3$CO$_2$H, increase the rate of reaction [3,4,7,9,10]. In the course of our investigations aimed at the development of novel catalyst/cocatalyst systems for hydroamination processes, we have found that the salts NH$_4$X (X$^-$ = low-coordinating anion) can strongly increase the reaction rate when Pd(II) complexes are used as catalysts in the addition of secondary amines to activated alkenes. We present here the results obtained exploring the catalytic potential of the complexes [Pd(acac)$_2$] (**1**) and [Pd(hfa)$_2$] (**2**) (hfa = hexafluoroacetylacetonate) in the presence of the NH$_4$X additive.

---

* Corresponding author. Tel.: +39 0432 558 840; fax: +39 0432 558 803.
E-mail address: alessandro.delzotto@uniud.it (A. Del Zotto).

0020-1693/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2005.03.035

The use of both complexes **1** and **2** as catalysts in hydroamination processes is unprecedented. As the closely related species [Pd(CF_3CO_2)$_2$] (**3**) has been shown to be an active hydroamination catalyst in the presence of a strong acid [3,10], while no data have been published on the use of [$Pd_3(CH_3CO_2)_6$] (**4**)/strong acids systems, our investigation on the role played by the ammonium salts has been extended to carboxylates **3** and **4**. Finally, the cyclometalated species [{Pd(C–N)(μ-CH_3CO_2)}] (**5**) [15] (C–N = 2-(2-pyridinylmethyl)phenyl-C^1,N) has also been tested as catalyst to compare its efficiency with that of the parent complex **4**. Recently, a mechanistic study of the hydroamination reaction of activated alkenes has revealed that protons generated by Lewis acid hydrolysis can be effective catalyst [14]. Thus, certain metal ions can act as a proton source rather than olefin activators through coordination of the C=C bond. At this regard, it should be noted that complex **4** has not found to be an effective proton generator [14].

2. Experimental

2.1. Instrumentation and analyses

The ^{1}H NMR spectra (at 200.13 MHz) were run on a Bruker AC 200 F QNP spectrometer and the chemical shifts were referenced to $SiMe_4$. The GC–MS analyses were carried out with a Fisons TRIO 2000 gas chromatograph–mass spectrometer working in the positive ion 70 eV electron impact mode. Injector temperature was kept at 250 °C and the column (Supelco SE-54 30 m long 0.25 mm i.d. coated with a 0.5 μm phenyl methyl silicone film) temperature was programmed from 50 to 310 °C with a gradient of 10 °C/min. The GC analyses were run on a Fisons GC 8000 Series gaschromatograph equipped with a Supelco® PTA-5 column [30 m long 0.53 mm i.d. coated with a 3.0 μm poly (5% diphenyl-95% dimethylsiloxane) film]; injector and column temperatures as indicated above.

2.2. Reagents and catalysts

The palladium compounds [Pd(acac)$_2$] (**1**), [Pd(hfa)$_2$] (**2**) and [$Pd_3(CH_3CO_2)_6$] (**4**) were purchased from Aldrich while [Pd(CF_3CO_2)$_2$] (**3**) was purchased from Fluka. The complex [{Pd(C–N)(μ-CH_3CO_2)}] (**5**) was prepared according to a published procedure [15]. All amines (purity 97–99+%) and alkenes (purity 95–99%) were purchased form Aldrich and used without further purification.

2.3. General procedure for the catalytic tests

The Pd(II) catalyst (33 μmol, 2 mol%) amine (1.65 mmol) and alkene (1 mL) were charged in the order into a 10 mL Schlenk which was immediately transferred into an oil bath thermostatted at 313 K, the solution being maintained under vigorous stirring. Samples for the GC analysis were extracted by syringe and suitably diluted with ethyl ether. When the cocatalyst was used, 33 μmol of NH_4PF_6 was added to the alkene solution already containing amine and catalyst. Working under inert atmosphere was not necessary.

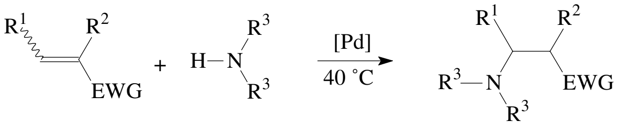
3. Results and discussion

3.1. General considerations

The reaction under investigation is depicted in Scheme 1. Activated alkenes (methacrylonitrile **6**, crotononitrile **7**, ethyl methacrylate **8**, ethyl *trans*-crotonate **9**, 2-cyclohexen-1-one **10** and *trans*-3-nonen-2-one **11**) have been combined with secondary amines (piperidine **12**, morpholine **13**, *N*-methylpiperazine **14**, methylbenzylamine **15** and methylcyclohexylamine **16**). In particular, the couple **6**/**12** has been chosen as model substrate for explorative trials. The reaction was conveniently performed at 40 °C, using the alkene as the solvent (alkene/amine molar ratio ~7) and usually 2 mol% catalyst. In the absence of a Pd(II) catalyst or any other additive, **6** and **12** gave only 13% of the hydroamination product after 24 h. Similar very low amounts of product, or in some cases a total lack of reaction, were observed for the other alkene/amine combinations.

In the present study, one of the main aims was the development of highly efficient cocatalysts which could be used instead of strong acids [3,4,10]. The first successful choice was the ammonium ion in that it behaves as a Brønsted acid and its salts are readily handling and soluble. To compare the cocatalytic effect of strong acids and ammonium salts, CF_3SO_3H and NH_4PF_6 have been suitably chosen and used in combination with complex **4**. As a matter of fact, the two additives gave analogous results. For example, for the standard reaction between **6** and **12** run with both catalyst and additive in 2 mol% concentration, the yield after 3 h was 96% and 93% using the ammonium salt or triflic acid, respectively. In accord with this finding, all the successive catalytic tests have been carried out using the ammonium salt as a powerful and easy to handle cocatalyst.

Interestingly, the addition of NH_4PF_6 to a mixture of **6**/**12** afforded a significant increase of the reaction rate even in the absence of a palladium(II) complex. Thus, the yield after 24 h increased from 13% to 61% using



Scheme 1.