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Co-catalysis for one-pot tandem hydroformylation-aldol condensation-hydrogenation with involvement of phosphino-phosphonium based bi-functional ligand and aniline

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ABSTRACT

Co-catalysis in the way of synergetic catalysis and sequential catalysis has emerged as a powerful tool to achieve one-pot tandem reaction. Herein, a tri-functional catalytic system containing phosphino-phosphonium bi-functional ligand (**L2**) based Rh-catalyst and aniline was developed for three-step tandem hydroformylation-aldol condensation-hydrogenation to produce ketones from olefins. It was found that the intramolecular bi-functionalities of phosphino-fragment and phosphonium [P(V)$^+$] in **L2** greatly facilitated hydroformylation due to their synergetic effect on activation of carbonyl (—C═O) in Rh-acyl intermediate. In addition, the phosphonium in **L2** also served as a Lewis acid to catalyse condensation of acetone with aniline to form enamine catalyst. The latter with more nucleophilicity was able to attack the aldehydes (formed from the preceding hydroformylation) to accomplish the subsequent aldol condensation along with the release of aniline. Finally, the obtained α,β-unsaturated ketones were hydrogenated to yield ketones over **L2**-based Rh-catalyst under the hydroformylation conditions. Such tri-functional catalytic system in combination of transition-metal catalysis, Lewis acid catalysis and enamine catalysis also exhibited good generality for the tandem hydroformylation-aldol condensation-hydrogenation of the different olefins to produce ketones.

1. Introduction

Hydroformylation of olefins to give aldehydes in the presence of Rh-catalysts constitutes one of the most intriguing and extensively studied reactions [1–5]. Owing to the versatile chemical properties of aldehyde group, the obtained aldehyde products are required to convert to more valuable and stable products such as alcohols, amines, acetals, aldol condensation products etc [2]. Following the atom economy and low energy consumption in green chemistry, combining hydroformylation with aldol condensation, hydrogenation or amination to form tandem reaction sequences directly under hydroformylation conditions have become a powerful and promising synthetic method [6–10]. Among them, hydroformylation/aldol condensation [8,10]. or hydroformylation/aldol condensation/hydrogenation [7] are significantly attractive one-pot synthesis of (α,β-unsaturated) ketones/aldehydes from olefins, which serve as valuable chemical compounds with broad applications in cosmetic, agrochemical, and pharmaceutical industries [2]. As for the involved aldol condensation classically using acids/bases as the catalysts, primary amines via forming enamine intermediates with ketones (aldehydes) have also been reported to serve as efficient catalysts specifically in the presence of metal Lewis acids [11–13].

Co-catalysis in combination of transition metal catalysis with organocatalysis has emerged as a powerful tool to achieve organic transformations that cannot be accomplished by either individuals, which has been widely reviewed in the literature [14–18]. For example, in simple physical mixing way, co-catalysis comprised of amine-based enamine catalysts and transition metal catalysts usually have shown unprecedented organic transformations over the past decade [14,16]. On the other hand, the uses of exquisitely designed bi-functional ligands serving as bridges between transition metal catalysis and organocatalysis have been observed to be successful in many hydroformylation-based tandem reactions as reported by Beller [19,20], Breit [21,22], Jin [23] etc., as well as exhibiting the intramolecular synergetic effects to dramatically improve the single reaction processes [24–29].

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Phosphonium [P(V)$^+$] cations are widely applied as the typical metal-free Lewis acids for a variety of C—C, C—O and C—N bond forming reactions [30,31], as well for activation of C=O bond in Baylis-Hillman reaction [32] and cyanosilylation of ketones [33]. Based on this know-how, we had developed several types of phosphino-phosphonium based bi-functional ligands for tandem hydroformylation/aetalization [34,35]. However, these in hand bi-functional ligands did not work in this studied tandem hydroformylation-aldol condensation-hydrogenation. With our continuous interests in tandem reaction sequences under hydroformylation conditions in the way of multi-functional co-catalysis, herein we disclosed a novel tri-functional system containing the phosphino-phosphonium bi-functional ligand (**L2**) and aniline, which was used together with Rh(acac)$(CO)_2$ to perform tri-functional co-catalysis in combination of Rh-phosphine transition metal catalysis, Lewis acid (phosphonium) catalysis, and enamine catalysis for tandem hydroformylation-aldol condensation-hydrogenation. In this tri-functional catalytic system, **L2**-based Rh-catalyst could effectively catalyse hydroformylation and hydrogenation. And the phosphonium [P(V)$^+$] itself served as a Lewis acid to catalyse the condensation of acetone with aniline to form enamine catalyst. The latter with more nucleophilicity was able to attack the aldehydes (formed from the preceding hydroformylation) to accomplish the aldol condensation along with the release of aniline.

2. Experimental section

2.1. Reagents and analysis

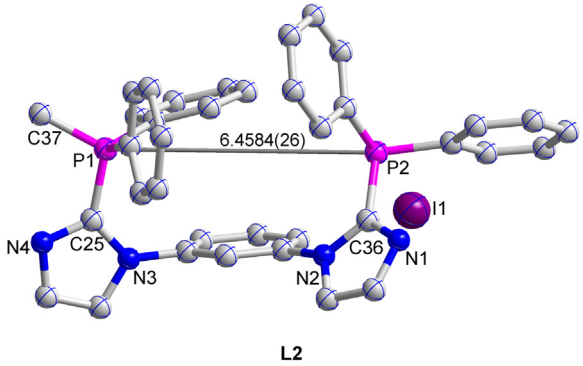
The chemical reagents were purchased from Beijing Innochem Science & Technology Co. Ltd. and Sigma-Aldrich China, and used as received. The UV–vis. spectrum was recorded on UV-2550 spectrophotometer. The ^{1}H NMR spectra for the analyses of the common compound was recorded on a Bruker Avance 400 spectrometer. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column (30 m × 0.25 mm × 0.25 μm). GC-mass spectrometry (GC–MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector.

2.2. Synthesis

The ligands of **L1–L4** were prepared according to the procedures reported by C. Chauvin [36] and us [34] before.

2.3. General procedures for hydroformylation-aldol condensation-hydrogenation of olefin in acetone

In a typical experiment, the commercial complex of Rh(acac)$(CO)_2$ (0.0025 mmol) and the pure **L2** (0.015 mmol) were sequentially added into the mixture of styrene (5 mmol, or the other olefin), aniline (5 mmol) and acetone (1.5 mL) in a 50 mL Teflon-lined stainless steel autoclave. The obtained mixture was sealed and pressured by syngas to 4.0 MPa. The reaction mixture was stirred vigorously at the appointed temperature for some time. Upon completion, the autoclave was cooled down to room temperature and depressurized carefully. The reaction solution was analysed by GC to determine the conversions (*n*-dodecane as internal standard) and the selectivities (normalization method). The products were further identified by GC-Mass.



L2

Fig. 1. The single crystal structures of **L2** (The hydrogen atoms are omitted for clarity) [34].

3. Results and discussion

The molecular structural of **L2** in Fig. 1 [34] indicated that the incorporated electron-rich phosphino-fragment and the Lewis acidic phosphonium are oriented compatibly without quenching problem. However, the only use of **L2**-based Rh-catalyst just sluggishly enabled the hydroformylation under the optimal conditions (P/Rh = 6 molar ratio, syngas 4.0 MPa, 120 °C) (Table 1). Obviously, the presence of acetone badly inhibited the hydroformylation of styrene. In 20 h only 20% conversion of styrene was obtained with 100% selectivity to the aldehydes (2-/3-phenylpropanals) (Entry 1). In contrast, in the absence of acetone, hydroformylation of styrene performed rapidly in 1 h over the same **L2**-based Rh-catalyst with 90% conversion of styrene (Entry 2). Evidently, acetone could serve as an O-containing ligand to coordinate with Rh-centre. The presence of excess acetone in the reaction system badly depressed the coordination of the phosphine ligand (in catalytic amount) to Rh-centre, which led to the decelerated hydroformylationy of styrene as observed in Entry 1.

The wide uses of primary amines such as aniline with the presence of Lewis acids [11–13] for efficient aldol condensation inspired us to introduce the third component of aniline into the **L2**-based Rh-catalyst. Interestingly, when aniline in equal amount to styrene (5.0 mmol) was used with **L2** (0.015 mmol) and Rh(acac)$(CO)_2$ (0.0025 mmol) together, the tandem transformation of styrene (5.0 mmol) to the required saturated ketones proceeded rapidly. 92% conversion of styrene was observed along with 100% selectivity to oxo-products including 7% phenylpropanals and 93% ketones (Entry 3, the branched 5-phenylhexan-2-one as the major product, B/L = 78/15). The product of branched phenylhexan-2-one was then isolated and analysed by ^{1}H NMR spectroscopy (see SI), in order to calibrate GC analysis as the authentic sample. The evolution process of styrene conversion and aldehyde/ketones selectivities against reaction time in Fig. 2 indicated that, in first 2 h, 78% styrene has already converted to the aldehydes. As time going on, the formed aldehydes gradually transformed to the aldol-products by condensing with acetone and then hydrogenated to the saturated ketones rapidly.

When *N*-methylaniline or *N*,*N*-dimethylaniline was applied instead of aniline, the selectivity to the ketones decreased seriously (Entries 4 and 5). Especially for tertiary *N*,*N*-dimethylaniline relatively with the strongest basicity, the aldol condensation of 2-/3-phenylpropanals with acetone was completely prohibited (Entry 5), implying that the expected aldol condensation was not catalysed by a base. However, even with the presence of aniline, the phosphonium-free ligands such as **L1**, **L3**, and PPh_3 only corresponded to the hydroformylated products (aldehydes) along with the universally observed by-products of imines formed from side-reaction of condensation of 2-/3-phenylpropanals with ani-