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Ruthenium-catalyzed hydroformylation of the functional unsaturated fatty nitrile 10-undecenitrile

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ABSTRACT

The hydroformylation of 10-undecenitrile (**1**), a route towards polyamide-12, has been studied using Ru-diphosphite catalysts. The reactions proceeded effectively by *in situ* combination of chloro precursors such as $RuCl_2(PPh_3)_3$ and $RuCl_2(DMSO)_4$ with Biphephos. High productivities (TON up to 15,000 mol(aldehyde) mol(Ru)$^{-1}$) were achieved by carrying the reactions at low catalyst loading ($[\mathbf{1}]_0/[Ru] = 20{,}000$), at 120 °C in toluene or acetonitrile under 20 bar CO/H_2 (1:1), with 20 equiv of Biphephos *vs.* Ru. Up to 75% chemoselectivity for the aldehydes and very high regioselectivities for the linear aldehyde ($l/b = 99{:}1$) were reached under such optimized conditions. Lower loadings of Biphephos (down to 2.5 equiv. *vs.* Ru) did not affect the chemo- and regioselectivities but the activity. The Ru-Biphephos combinations showed a non-optimized hydroformylation TOF_{HF} of *ca.* 2–7 min^{-1}, that is *ca.* 1–2 order of magnitude lower than that of analogous Rh-based systems ($TOF_{HF} = ca.$ 80 min^{-1}). These Ru-Biphephos systems are, however, incapable, under the conditions suitable for selective hydroformylation, to promote isomerization of internal olefins, and hence to achieve a tandem isomerization-hydroformylation process.

1. Introduction

If rhodium is irrefutably the most efficient metal to promote olefin hydroformylation, one of the most widely applied homogeneously-catalyzed processes in industry [1], its very high and volatile price has urged investigation on other metals [2]. In 1977, the relative activities of the unmodified metal carbonyl complexes in hydroformylation were suggested as follows: Rh ≫ Co > Ir, Ru > Os > Pt > Pd ≫ Fe > Ni [3]. However, recent reports have shown that those old assumptions should be re-examined; for instance, the activity ratio of rhodium-to-iridium is in fact much closer to 1 than the 10,000:1 ratio initially predicted [4,5]. Ruthenium may also offer an interesting compromise between price and activity, as it is currently *ca.* 15 and 12 times cheaper than rhodium and iridium, respectively [6], and its activity in an oxo process is generally announced as one of the best (with iridium) among all alternative metals.

The first investigations on Ru-catalyzed hydroformylation began as early as in 1965 with Wilkinson's brief report on hydroformylation of 1-pentene using the mononuclear zerovalent complex $Ru(CO)_3(PPh_3)_2$ as catalyst precursor (100–120 °C, 100 bar, $CO/H_2 = 1{:}1$) [7]. The authors subsequently presented more detailed results for 1-hexene hydroformylation with the same catalyst system and other related mononuclear Ru-phosphine complexes; at a quite high catalyst loading ([olefin]/[Ru] = 100), the turnover frequency (TOF) reached 0.075 min^{-1}, with a claimed 100% chemoselectivity for the aldehydes in most cases, although the linear-to-branched ratio was low ($l/b = 2.0$–2.9) [8]. The Ru(II) dihydrido dicarbonyl complex $Ru(H)_2(CO)_2(PPh_3)_2$ was proposed as the principal active species. $Ru_3(CO)_{12}$ proved to be a modest precursor (24% conv.) under the studied conditions but increased conversion was obtained upon addition of 1 equiv. (*vs.* Ru) of PPh_3 (88% conv.) or, even better, $P(OPh)_3$ (95% conv.); however, those systems were all less active than the mononuclear complexes. Meanwhile, Schulz and Bellstedt also reported hydroformylation of propylene with $Ru_3(CO)_{12}$ to afford 94% of conversion, but the final mixture contained less than 25% of aldehydes [9].

Examples of 1-hexene hydroformylation conducted in an ethanol-water (80:20) mixture using water-soluble complexes of the type K[Ru(EDTA-H)Cl] were reported in 1988 [10]. At a high catalyst loading ([olefin]/[Ru] = 140; 130 °C, 50 bar CO/H_2 1:1), these

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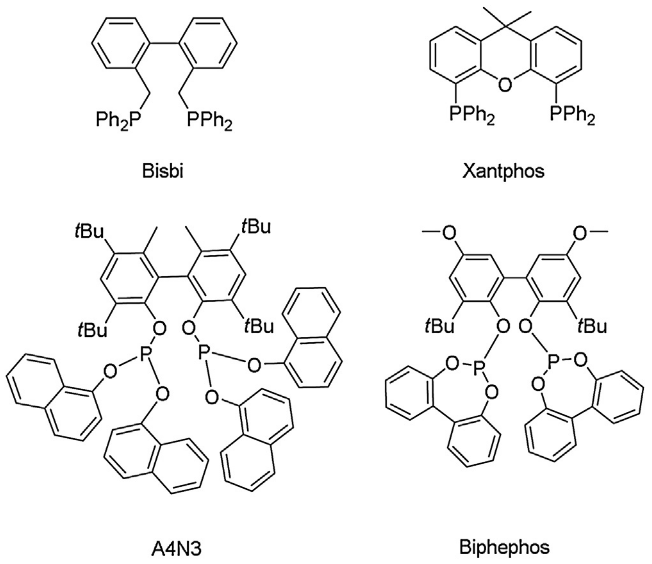

Fig. 1. Diphosphine and diphosphite ligands used for ruthenium-catalyzed hydroformylation.

led to full conversion of the olefin (overall TOF = 0.2 min^{-1}) and exclusive formation of linear heptanal.

Surprisingly, ruthenium-catalyzed hydroformylation with the ligands most often used nowadays in combination with rhodium, *i.e.* diphosphines and diphosphites, was not reported until recently. It is only in 2012 that Nozaki and coworkers reported on combinations of $\{RuCp(acac)\}_2$ with Xantphos or Bisbi diphosphines, or the A4N3 diphosphite (Fig. 1) [11]. The latter diphosphite ligand allowed reaching increased chemo- (up to 66% aldehydes) and regioselectivities (*l*/*b* up to 79) in the hydroformylation of 1-decene (100 °C, 20 bar CO/H_2 1:1); the side-products were essentially isomerized (internal) olefins (19%) and a slight amount of the hydrogenation product (1.5%). The catalyst loading was, however, quite high ([olefin]/[diphosphite]/[Ru] = 40:2:1) and overall TOFs were about 0.025 min^{-1}.

Domino hydroformylation-hydrogenation reactions, to end up with the corresponding alcohols instead of the aldehydes, were also developed. Besides examples relying on rhodium complexes to achieve hydroformylation and ruthenium complexes for the hydrogenation reaction [11,12], Beller and coworkers developed the first such domino reaction with the same ruthenium catalyst. Using $Ru_3(CO)_{12}$ or Ru(methylallyl)$_2$(COD) as precursor, combined with 1 equiv. (*vs.* Ru) of a 2-phosphino-substituted imidazole ligand, at a [olefin]/[Ru] ratio of 167, 130 °C and 60 bar CO/H_2 (1:5), they achieved full conversion of 1-octene (overall TOF = 0.13 min^{-1}) to provide 87% of alcohol (*l*/*b* = 10), along with 9% of octane and less than 1% of the intermediate aldehyde [13,14].

In previous studies, we reported the use of Rh-Biphephos [15] and Ir-Biphephos [5][5c] catalyst systems for the tandem isomerization-hydroformylation [16,17] of the unsaturated fatty nitrile 10-undecenitrile (**1**) (Scheme 1), as a route toward biosourced polyamide-12. Those systems performed at very high substrate-to-catalyst ratio (20,000–100,000) and yielded the desired linear aldehyde (**2**) with high chemo- and regioselectivities up to 93% and 99%, respectively. However, significant amounts of undesired isomerization products (**1-*int-x***) along with minute amounts of the hydrogenation product (**4**) were formed, which eventually plague both conversions and selectivities for the desired linear aldehydes (Scheme 1). Preliminary experiments showed that potentially interesting results could be also reached with ruthenium catalysts, although the activities were apparently much lower [5][5c]. Herein we report full details on the isomerization-hydroformylation of 10-undecenitrile with such ruthenium-based systems. A variety of precursors and ligands, as well as regular reaction parameters (solvent, temperature, syngas pressure, substrate concentration), have been screened.

2. Experimental

2.1. General features

All reactions involving Ru-phosphine catalysts were performed under an inert atmosphere (argon) using standard Schlenk techniques. Solvents (toluene, THF, etc.) were purified over alumina columns using a MBraun system. $RuCl_2(PPh_3)_3$, $RuCl_2$(*p*-cymene) and $Ru_3(CO)_{12}$ were generously provided by Umicore Co. and stored in the glove box. $RuCl_2(DMSO)_4$ was synthesized according to the literature procedure. [18] Biphephos and A4N3 diphosphite ligands were purchased from Strem Chemicals and MCAT, respectively, and used as received (stored in the glove box). 10-Undecenenitrile (typically 94% pure, contains 6% of 9-undecenitrile (**1-*int-0***) and other internal isomers (**1-*int-x***), as determined by NMR) was supplied by Arkema; it was first eluted through a short alumina column and vacuum-distilled (Kügelrohr distillation) at 125 °C under 0.03 mm Hg prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-300 and AM-400 spectrometers. ^1H and ^{13}C chemical shifts were determined using residual signals of the deuterated solvents and were calibrated *vs.* $SiMe_4$.

2.2. General procedure for hydroformylation reaction

In a typical experiment, the ruthenium precursor $RuCl_2(PPh_3)_3$, as a 1.0 g L^{-1} toluene solution (0.72 mL, 0.75 μmol) was added on Biphephos (11.8 mg, 15.0 μmol) in a Schlenk flask. 10-undecenitrile (2.479 g, 15.0 mmol) in the desired solvent (toluene or acetonitrile, 15 mL) was added onto the resulting mixture. The solution was transferred under argon into a 90 mL stainless-steel autoclave under argon, equipped with a magnetic stir bar cross. The reactor was sealed, charged with CO/H_2 at the desired pressure at room temperature, stirred (800 rpm) and then heated with silicon oil set at the desired temperature. During the reaction, aliquots were sampled at regular time intervals to monitor the conversion and selectivities by NMR. After the appropriate reaction time, the reactor was cooled to room temperature and vented to atmospheric pressure. The solution was analyzed by NMR (after evaporation of solvent). The conversion of **1** into **1-*int-x*** and **2–5**, as reported in Tables 1–5, was calculated taking into account the quantity of internal isomers (**1-*int-x***) initially present in the substrate: $\mathrm{Conv}(\mathbf{1}) = ([\mathbf{2}]_t + [\mathbf{3}]_t + [\mathbf{4}]_t + [\mathbf{5}]_t + [\mathbf{1\text{-}int\text{-}x}]_t - [\mathbf{1\text{-}int\text{-}x}]_0)/[\mathbf{1}]_0$. The reported TOF values are overall values calculated from the conversion at total reaction time: TOF = conv × 20,0000/time.

The NMR characteristics for 10-undecenenitrile (**1**), its internal isomers (**1-*int-x***), the hydroformylation products (**2** and **3**) and the hydrogenation product (**4**) have been reported previously [5,15][5c,15]. Typical ^1H NMR signals for the linear alcohol (**5**) were observed at δ = 3.62 (t, *J* = 6 Hz, 3H, $HOCH_2CH_2$-) ppm.

3. Results and discussion

First hydroformylation experiments were performed at low catalyst loading ($[\mathbf{1}]_0$/[Ru] = 20,000; initial **1**/**1-*int-x*** ratio = 94:6) using different chloro Ru(II) ($RuCl_2(PPh_3)$, $RuCl_2$(*p*-cymene), $RuCl_2(DMSO)_4$) and Cl-free Ru(0) ($Ru_3(CO)_{12}$) precursors in combination with Biphephos, diphosphite A4N3 or triphenylphosphite. For the sake of comparison, the experimental conditions used were those optimized in the hydroformylation of **1** using Rh(acac)(CO)$_2$-Biphephos [15].