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Hydroformylation-hydrogenation and hydroformylation-acetalization reactions catalyzed by ruthenium complexes

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This paper is dedicated to Prof. Georgiy B. Shul'pin.

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ABSTRACT

In this work, the catalytic activity of ruthenium II and III complexes containing chloride, pyridine, phosphine and CO ligands was investigated in the hydroformylation – hydrogenation and hydroformylation – acetalization reactions. The complexes *mer*-[$RuCl_3$(dppb)(H_2O)]**(1)**, *mer*-[$RuCl_3$(dppb)(4-Vpy)]**(2)**, *mer*-[$RuCl_3$(dppb)(4-*t*Bupy)]**(3)**, *mer*-[$RuCl_3$(dppb)(py)]**(4)**, *mer*-[$RuCl_3$(dppb)(4-Phpy)]**(5)**, *mer*-[$RuCl_3$(dppb)(4-Mepy)]**(6)**, *cis*-[$RuCl_2(CO)_2$(dppb)]**(7)**, *trans*-[$RuCl_2(CO)_2$(dppb)]**(8)**, $RuCl_3 \cdot xH_2O$**(9)**, [$RuCl_2(PPh_3)_3$]**(10)** and [$RuCl_2(PPh_3)_2$(dppb)]**(11)** were used as supplied or synthesized as previously described in the literature {Where PPh_3 = triphenylphosphine, dppb = 1,4-bis(diphenylphosphino)butane, py = pyridine, 4-Mepy = 4-methylpyridine, 4-Vpy = 4-vinylpyridine, 4-*t*Bupy = 4-*tert*-butylpyridine and 4-Phpy = 4-phenylpyridine}. These complexes were used as a pre-catalysts in a hydroformylation catalytic system to produce C—C, C=O and C—O bonds, where 1-decene resulted in a formation of respective alcohol and dimethyl acetals. Several reactions were performed in order to find the best reaction conditions presenting the best conversion (64% after 24 h). The 1-decene was also used as a substrate in two type tandem reactions labeled as: hydroformylation – hydrogenation (HH) and hydroformylation – acetalization (HA) reactions. The relationship between Ru – catalyst/substrate was 1:100, without free ligands or additives, in a controlled temperature and pressure. All the products of catalytic reactions HH and HA were analyzed by CG-FID with good yields.

1. Introduction

Transition-metal-catalyzed hydroformylation reactions constitute one of the most powerful tools for C—C bond formation in organic synthesis of aldehydes [1]. Aldehydes are valuable final products and intermediates in the synthesis of bulk chemicals such as alcohols, esters, acetals and amines. Aldehydes, acetals and alcohols are important aroma compounds used as ingredients in numerous perfumes, flavors and foods [2]. Nowadays, millions of tons of olefins are converted into aldehydes by hydroformylation reactions. Not only are aldehydes of enormous importance as constituents of flavoring mixtures, but they are also products, which can be easily derived from these compounds such as hemiacetals, acetals or carboxylic acids and their esters. Special hydroformylation protocols allow the one-step production of alcohols, which are also of crucial importance as aroma compounds [3,4]. Scheme 1 describes the general route to prepare aldehyde, alcohol and dimethylacetal by a hydroformylation – hydrogenation and hydroformylation – acetalization reactions catalyzed by ruthenium complexes.

In 1969 A.E. Shilov and co-workers showed that transition metal complexes, such as Pt (II), can catalyze H/D exchange of alkenes with solvent protons in homogeneous solution, thereby laying the foundation for the now successful field of activation of C—H bond [7–9]. The substantial isolation of the products of oxidative addition of alkanes to transition metals was first achieved by Bergman [10]. In toward of this view, very few [M(hydrido)(σ-alkyl)] complexes are know, as they tend to undergo spontaneous elimination of the alkane, which represents a step in the mechanism of the

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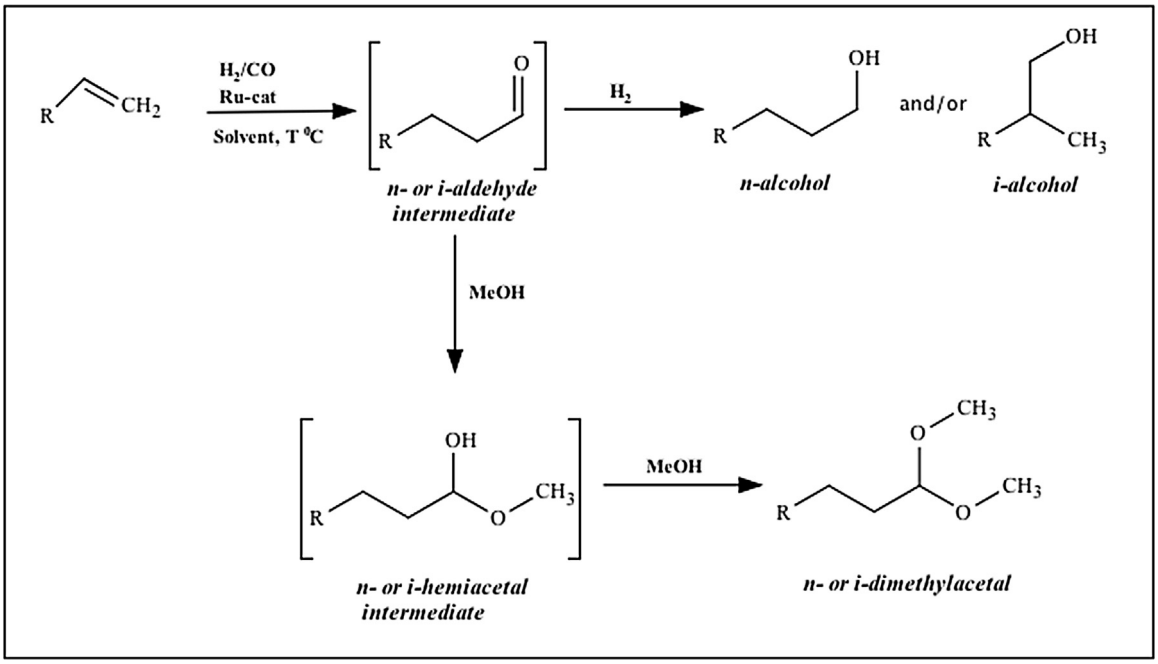

Scheme 1. Hydroformylation – hydrogenation (HH) and hydroformylation – acetalization (HA) reactions catalyzed by ruthenium complexes [5].

homogeneous catalytic hydrogenation of alkenes [6]. As a result, the activation of terminal $=CH_2$ group by transition metal complexes has the net effect of moving the C=C group along the chain of the molecule [11]. This is frequently a side reaction, desired or not according to circumstances, in other types of catalytic alkene reaction, such as hydrogenation or hydroformylation reactions. The mechanism of alkene isomerization can occurs by two different pathways, one by alkyl route, which require an M—H bond and a vacant site; and other one by allyl mechanism, which is adopted by a metal fragment that have two vacant sites but no hydrides [11] . In brief, in both mechanisms occur a C—H activation, where the transition metal complexes are capable of catalyzing the 1,3-migration of hydrogen substituent on alkene.

Ruthenium complexes have been applied to homogeneous hydroformylation reactions, as catalysts or pre-catalysts, since 1965 by Wilkinson and co-workers [12]. Since then, several ruthenium complexes containing varying ligands, such as CO, have been reported [13,14]. In the literature, hydroformylation reactions catalyzed by ruthenium complexes using different phosphines as free ligands and other additives, e.g. LiCl, are occasionally quoted [1,15]. Therefore, one of the main aims of this research was to attempt to minimize the use of free ligands and additives in order to generate minimal residues in the synthesis of alcohols and acetals, using olefins as precursors.

In a previous study, our group published the syntheses, characterization and catalytic activity of *mer*-[$RuCl_3$(dppb)(N)] (where N = derivatives pyridine ligands), in the hydrogenation of cyclohexene, undecanal and cyclohexane carbaldehyde in non-aqueous solutions [16].

Herein the catalytic activity of ruthenium II and III complexes is described, in the tandem type reactions labeled as: hydroformylation – hydrogenation (HH) and hydroformylation – acetalization (HA). Different reaction conditions were used, which include different organic substrates, solvents, temperature and pressure to produce aldehydes, alcohols and acetals.

2. Experimental section

2.1. Materials and methods

Solvents were purified by standard methods. All reagents used were of reagent grade or comparable purity, which were supplied from commercial sources: $RuCl_3 \cdot xH_2O$, triphenylphosphine (PPh_3), 1,4-bis(diphenylphosphino)butane (dppb), pyridine (py), 4-methylpyridine (4-Mepy), 4-vinylpyridine (4-Vpy), 4-*tert*-butylpyridine (4-*t*Bupy) and 4-phenylpyridine (4-Phpy) were used as received from Aldrich. All complexes used as pre-catalysts in this research were prepared as described in the literature: *mer*-[$RuCl_3$(dppb)(H_2O)]**(1)** [17], *mer*-[$RuCl_3$(dppb)(4-Vpy)]**(2)** [18], *mer*-[$RuCl_3$(dppb)(4-*t*Bupy)]**(3)** [18], *mer*-[$RuCl_3$(dppb)(py)]**(4)** [18], *mer*-[$RuCl_3$(dppb)(4-Phpy)]**(5)** [18], *mer*-[$RuCl_3$(dppb)(4-Mepy)]**(6)** [18], *cis*-[$RuCl_2(CO)_2$(dppb)]**(7)** [19], *trans*-[$RuCl_2(CO)_2$(dppb)]**(8)** [19], $RuCl_3 \cdot XH_2O$**(9)**, [$RuCl_2(PPh_3)_3$]**(10)** [20] and [$RuCl_2(PPh_3)_2$(dppb)]**(11)** [21]. For the synthesis of the hydride-ruthenium-CO complex **(7′)**, the *cis* complex **(7)** was stirred under H_2 atmosphere for 24 h in a Schlenk flask. The yellow solid was filtered off and dried in vacuum. [HRuCl$(CO)_2$(dppb)] **(7′)**: Yield: 90%. Calc. for $C_{30}H_{29}ClO_2P_2Ru$: C, 58.11; H, 4.71%. Found: C, 58.07; H, 4.78%. $^{31}P\{^1H\}$ s = 8,50 ppm and 1H *t* = −10.5 ppm and IR (KBr) ν(Ru-CO) 2065 and 2008 cm^{-1} and ν(Ru-H) 1952 cm^{-1}.

2.2. Instrumentation

Elemental analyses were performed in a Fison EA 1108 model. The FTIR spectra of the powder complexes were recorded from KBr pellets in the range of 4000 and 200 cm^{-1} range, in a Bomen-Michelson FT MB-102 instrument.

The catalytic experiments were carried out in a HEL 8 × 16 mL parallel reactor.

All NMR experiments were recorded on BRUKER DRX400 MHz equipment; in a BBO 5 mm probe at 298 K, using $CDCl_3$ (^1H) and