



Ruthenium carbonyl-complex catalyzed hydroaminomethylation of olefins with carbon dioxide and amines

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ABSTRACT

Use of carbon dioxide as a reactant instead of toxic carbon monoxide in the hydroaminomethylation reaction sequence is demonstrated for the first time. The present $\text{Ru}_3(\text{CO})_{12}$ -catalyzed one-pot protocol includes reverse-water-gas-shift (RWGS) reaction, hydroformylation reaction and reductive amination which finally leads to secondary and tertiary amine. The influence of various reaction parameters including the effects of catalytic promoters and phase-transfer-catalysts has been investigated. Finally, an optimum reaction conditions were found by suppressing the major side products to have a variety of amines in excellent yields (up to 98%).

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1. Introduction

Presently, research interests in the area of organic syntheses are focussing on versatile and selective synthetic routes to manufacture useful and complex products from inexpensive feedstocks, a topic which is essentially driven both from economical and environmental perspectives. The substitution of toxic carbon monoxide (CO) from various reactions by naturally abundant, non-toxic and inexpensive carbon dioxide (CO_2) [1] appears to be an attractive option, in this regard. Literature reveals plenty of reports for the synthesis of useful compounds from CO_2 , such as carbonates [2], carbamates [3], urethanes [4], lactones [5], pyrones [6] and various acids-derivatives [7]. Among the variety of compounds synthesized from CO_2 , urea [8] is manufactured from CO_2 in the range of 100 million tons/year. Reduction of CO_2 and its synthetic use in C–C-bond forming reactions, however, may be one of the options for reducing atmospheric carbon dioxide and mitigating its “green-house effects”. Additionally, the significance of the concept for utilization of CO_2 becomes even more advantageous if CO_2 can replace its toxic but more reactive competitor carbon monoxide

(CO) as a C_1 -building block via reverse-water-gas-shift reaction (RWGS) [9] for many C–C bond forming processes.

Recently, a new hydroformylation route, involving RWGS reaction, was investigated by Tominaga and co-workers [10] which replaces CO by CO_2 as a reactant. The successful hydroformylation of various olefins leading to the corresponding alcohols was carried out at 80 bar pressure and 140 °C temperature using ruthenium cluster complex $\text{Ru}_3(\text{CO})_{12}$, as a catalyst precursor and LiCl as a promotor in *N*-methyl-2-pyrrolidone (NMP) as the solvent. This concept was further improved by using different ionic liquids [11] as solvents for easy separation of the products. For example, the mixed ionic liquid [bmim][Cl + NTf₂] [12] at higher temperatures (160 °C) allows shorter reaction times. Haukka and co-workers [13] have investigated the effect of ruthenium carbonyl-based catalysts and the role of promoters for hydroformylation of 1-hexene with CO_2 as a reactant at 60 bar pressure and 150 °C.

Synthesis of amines in comparison to many other functional groups in organic chemistry has received increasing attention [14,15]. Besides their industrial applications as bulk chemicals, due to their attractive biological activities, secondary and tertiary amines in particular are important targets, e.g. in drug discovery [16]. With the emergence of more and more biologically active nitrogen containing molecules, there is an increasing need for inexpensive and efficient synthetic methods to prepare amines as useful intermediates or target compounds [14]. In this regard, the hydroaminomethylation protocol offers an atom-efficient and convenient route to produce secondary and tertiary amine in a

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'one-pot' procedure by the reaction of olefins and primary or secondary amine in the presence of syn-gas.

Therefore we have focussed our efforts towards an extension of hydroaminomethylation from carbon monoxide to carbon dioxide based versions. To the best of our knowledge application of CO₂ as a reactant, for the hydroaminomethylation reaction, is not reported so far. Here, we report first examples of selective syntheses of various amines in excellent (up to 98%) yields *via* ruthenium cluster complex catalyzed hydroaminomethylation of olefins using CO₂ as a reactant.

2. Results and discussion

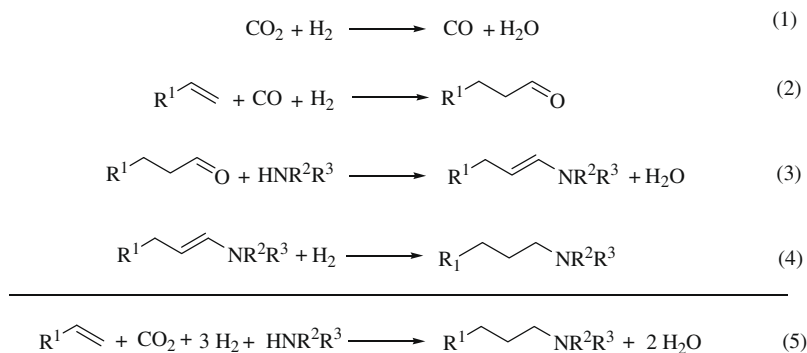
Hydroaminomethylation of olefins with syn-gas and amines involves three individual reaction steps, starting with hydroformylation of an olefin, followed by condensation of the resulting aldehyde with an amine to form an enamine or imine [14] and a final hydrogenation to give a secondary or tertiary amine. Hydroaminomethylation of olefins with hydrogen and CO₂ replacing CO requires a fourth reaction step and starts with the formation of CO and water by metal-catalyzed RWGS [9] (Eq. (1), Scheme 1). The *in situ* formed CO then undergoes conventional hydroformylation with the olefin and hydrogen (Eq. (2), Scheme 1) and finally

reductive amination occurs as discussed above (Eqs. (3) and (4), Scheme 1).

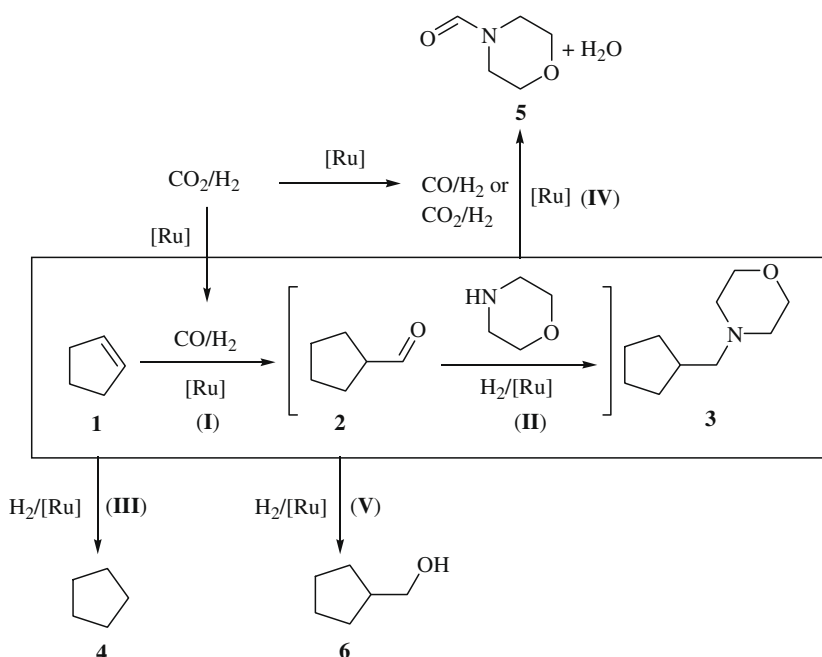
During this sequence, in addition to the formation of amines, various side-reactions like olefin hydrogenation, aldehyde reduction, amine formylation to formamides [17] are possible. Hydrogenation of olefins can be suppressed by using LiCl [10–12] as a promotor and the reduction of the intermediate aldehyde to alcohols should be suppressed with the added primary and secondary amines trapping the aldehydes in a condensation reaction once these are formed. Formylation of primary and secondary amines (with carbon dioxide and hydrogen), is to be suppressed by tuning the appropriate reaction conditions.

In order to elaborate the optimum reaction conditions for an efficient hydroaminomethylation of olefins with hydrogen, carbon dioxide and amines cyclopentene (1) and morpholine were taken as model substrates to give *N*-cyclopentylmethyl-morpholine (3) (reaction pathways I and II, Scheme 2).

After initial screening the experiments were carried out using the Ru₃(CO)₁₂ cluster complex as catalyst together with a promotor at 160 °C in toluene as a solvent. The conditions had to be more severe than normally used in hydroaminomethylation. This is mainly due to the reduction step from CO₂ to CO (RWGS reaction) requiring higher reaction temperatures and pressure [9].



Scheme 1. Hydroaminomethylation of olefins with CO₂.



Scheme 2. Reaction pathways of hydroaminomethylation of cyclopentene with CO₂ and possible side reactions.

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